

FINAL REPORT–NITRATE REMOVAL
DEMONSTRATION PROJECT

MINE WASTE TECHNOLOGY PROGRAM
ACTIVITY III, PROJECT 4

Prepared by

MSE Technology Applications, Inc.
200 Technology Way
P.O. Box 4078
Butte, Montana 59702

Prepared for

U.S. Environmental Protection Agency
Office of Research and Development
National Risk Management Research Laboratory
Cincinnati, Ohio 45268
IAG ID No. DW89935117-01-0

and

U.S. Department of Energy
Federal Energy Technology Center
Pittsburgh, Pennsylvania 15236
Contract No. DE-AC22-96EW96405

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REVIEWS AND APPROVALS:

Prepared by: Randy Hecht
Project Engineer

Reviewed by: Martin Foote
Project Manager

Approved by: Leighton J. Barry
Program Manager

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Executive Summary

The presence of nitrate in streams and groundwater can have detrimental effects on human health and the environment. Subsequently, state and federal water regulatory agencies have established limits of nitrate concentration in mine waste effluent waters. To date, the mining industry has relied principally on ion-exchange and reverse osmosis technologies for the removal of nitrates in their wastewater. Both of these technologies generate a concentrated nitrate brine that requires disposal.

The purpose of this project was to demonstrate nitrate removal technologies that had the potential to be more economical than conventional technologies and that would reduce or eliminate by-product wastestreams. To this end, a pilot-scale demonstration project was designed to combine conventional ion-exchange and innovative technologies in a process test train.

Following a selection process, three technologies were selected for the demonstration: 1) an ion-exchange unit furnished by Altair Equipment Company, Inc.; 2) an electrochemical ion-exchange unit furnished by Selective Environmental Technologies, Inc. (Selentec); and 3) a biological denitrification fixed film reactor furnished by Montana Tech of the University of Montana. The objectives of the evaluation were to compare performance claims by the developers with test results, ensure a minimum waste byproduct, determine feasibility for upscaling, and measure operational economics.

The field demonstration was conducted at the Mineral Hill Mine, an operating gold mine in Jardine, Montana, that is located adjacent to Yellowstone National Park and is owned and operated by TVX Gold Co., Inc. The source of the nitrate-laden water used for the demonstration was an historical portal that was one of the original mine entrances. The majority of the nitrate in the water is believed to come from the historic and present use of ammonium nitrate-fuel oil explosives.

The Nitrate Removal Demonstration Project was completed during 1996. Of all the technology combinations tested, biological denitrification of concentrated nitrate brine was the most successful at meeting the project goals to remove nitrate to less than 10 milligrams per liter (mg/L) and to minimize by-product waste.

Due to funding and equipment delivery delays, most of the testing was conducted during the early part of 1996, and extremely cold weather caused the mine water inlet pipe to freeze periodically. The freezing problem was finally alleviated; however, the testing was delayed by the frequent shutdowns. With warmer weather, large quantities of silt appeared in the mine portal discharge. This was not anticipated and caused numerous delays while filtering mechanisms were installed.

The conventional ion-exchange unit worked well and removed nitrate from the mine water very effectively. Input levels of 20 to 40 mg/L nitrate as nitrogen ($\text{NO}_3\text{-N}$) were typically reduced to less than 1 mg/L. The unit also produced a concentrated brine with the predicted levels of nitrate and chloride. Frequent equipment shutdowns and muddy mine water did not affect the operation of this unit to severely.

Biological denitrification was performed on both mine water and concentrated brine. This process worked well to eliminate nitrate in brine. Except for two process upsets (one caused by a large

concentration increase), nitrate was removed to levels less than 10 mg/L NO₃-N. This removal rate met the project goals and was typically greater than 99%.

Biological denitrification of the raw mine water was less successful, with a typical removal rate of 50%. This data was taken from an operating denitrification reactor at the mine. Past data had shown this reactor was very effective at nitrate removal; the frequent shutdowns and startups apparently had a detrimental effect.

Electrochemical ion exchange was unsuccessful at removing much nitrate from the concentrated brine because of the presence of high concentrations of a competing anion—chloride. Even though the ion-exchange resin had a high affinity for nitrate ions, the extremely high ratio of chloride ions to nitrate caused a continuous regeneration of the resin back to the chloride form and very little collection of nitrate.

Electrochemical ion exchange was able to remove nitrate from the raw mine water more effectively than from the brine. Nitrate was removed at first; however, fouling of the resin by dirty water occurred quickly, and the process was rendered ineffective after one batch. Filters were installed to alleviate the problem, but the size and nature of the particles made filtration difficult. Midway through the test sequence, the dirty resin was removed and replaced with clean resin. This worked temporarily; however, the resin was quickly fouled and rendered ineffective.

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1. Introduction

This document is the final report for the Mine Waste Technology Program (MWTP), Activity III, Project 4, Nitrate Removal and Destruction Project. The MWTP is funded by the U.S. Environmental Protection Agency (EPA) and is jointly administered by the EPA and the U.S. Department of Energy (DOE) through an Interagency Agreement. See the project organizational chart in Figure 1-1. This report details the project preparation, technology selection, site selection, field testing, and final results. The project was a field demonstration of conventional and innovative technologies combined in a manner to economically remove nitrate from mine wastewater while eliminating concentrated nitrate wastes.

1.1 Purpose

The purpose of this demonstration was to evaluate the ability of various technologies and combinations of technologies to treat a nitrate-laden mine effluent stream economically.

Success was defined as follows:

- treatment of a mine effluent to meet the national primary drinking water standard of 10 milligrams per liter (mg/L) $\text{NO}_3\text{-N}$ (this is the concentration of the nitrogen component of the nitrate ion);
- cost savings, compared to conventional ion exchange, demonstrated by incorporating operating and capital costs into a present-value analysis; and
- 80% reduction of by-product wastes, compared to conventional ion exchange.

1.2 Project Schedule

Field testing began on December 4, 1995, with the arrival of the ion-exchange unit and concluded on June 15, 1996. Prior to field testing, small-scale laboratory testing was performed by Montana

Tech of the University of Montana (Montana Tech) on the biological denitrification (or biodenitrification) system and by Selective Environmental Technologies, Inc. (Selentec), on the electrochemical ion-exchange unit. Field testing was divided into five separate demonstrations:

1. Ion exchange using raw mine water.
2. Biodenitrification using raw mine water.
3. Biodenitrification using concentrated brine produced by the ion-exchange unit.
4. Electrochemical ion exchange (EIX) using raw mine water.
5. Electrochemical ion exchange using concentrated brine produced by the ion-exchange unit.

Sampling for the majority of the tests did not begin until March 25, 1996, due to problems encountered with freezing water lines. Significant delays also occurred during the demonstration because of turbidity in the water caused by spring runoff and normal mining operations. A schedule of activities associated with the Nitrate Removal and Destruction Demonstration are presented in Table 1-1.

1.3 Report Structure

This final report has been organized in a systematic fashion to assist the reader with the review. Starting with the predemonstration activities of the project, the document continues through the demonstration site description, the technology description, experimental test design, data management and analysis, and finally the evaluation. Other pertinent information concerning laboratory performance, field sampling and analysis, and personnel qualifications are also provided. Supporting documentation is located in Appendices A and B.

Table 1-1. Demonstration task schedule.

Event	Date	Note
Technology Selection	May 1993	Three selected
NEPA Categorical Exclusion	January 1994	Approved
Demonstration Site Selection	February 1994	Mineral Hill Mine, MT
Quality Assurance Project Plan	October 1995	Approved
Health and Safety Plan	September 1995	Approved
Hazards Classification	September 1995	Nonhazardous
Demonstration Site Preparation	25 October 1995	Support Equipment Installed
Demonstration Field Test Plan Developed	November 1995	Approved
Nitrate Ion-Exchange Baseline Test Series	25 March 1996	4 Batch Tests
Biological Denitrification Test Series (Brine)	13 May 1996	Continuous Flow
Biological Denitrification Test Series (Water)	15 May 1996	Continuous Flow
Electrochemical Ion-Exchange Test Series (Brine)	19 March 1996	14 Batch Tests
Electrochemical Ion-Exchange Test Series (Water)	27 March 1996	12 Batch Tests

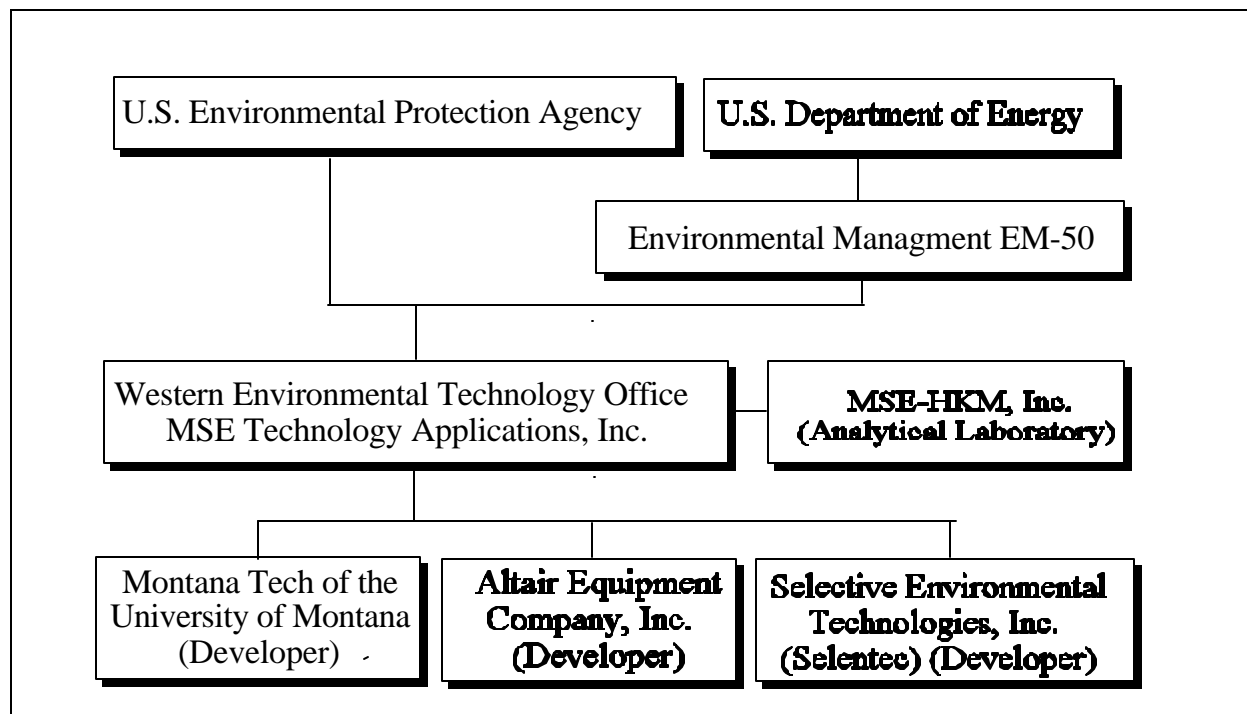


Figure 1-1. Project organizational chart.

2. Demonstration Participants And Responsibilities

Organizations involved in the technology demonstration are identified, and the primary responsibilities of each organization are described below.

2.1 Demonstration Participants

The organization and execution of the Nitrate Destruction and Removal Project was a collaborative effort between the technology developers and support organizations listed in Tables 2-1 and 2-2.

2.2 Responsibilities

Demonstration of the technologies was conducted by the developers with support and verification from MSE Technology Applications, Inc. (MSE), under the guidelines of the quality assurance project plan (QAPP) and the Demonstration Test Plan (Ref. 1, 2). Specific responsibilities are outlined in the following paragraphs.

2.2.1 MSE Technology Applications

MSE, in consultation with the EPA technical lead, was responsible for the following elements of the Nitrate Removal and Destruction Demonstration:

- designing and preparing the demonstration plan;
- selecting technologies to be demonstrated;
- selecting a suitable demonstration site;
- compiling site characterization information;
- securing physical and legal access to the site;
- developing the QAPP;
- developing a project hazards classification;
- developing a project health and safety plan;
- designing and installing demonstration process support equipment;
- providing logistical support for the on-site field demonstration;
- developing contracts for the design, construction, procurement, and leasing of demonstration equipment;

- developing operational schedules and demonstration test plans;
- obtaining federal, state and county permits and authorizations necessary to conduct the demonstration;
- documenting the experimental methodology and operation of the technology;
- training operational and sampling personnel;
- performing on-site sampling and analysis activities, including collection, homogenization, duplication, packaging, labeling, storing, and shipping of samples;
- selecting and verifying a qualified analytical laboratory for demonstration quality assurance (QA) sample analysis;
- managing, evaluating, interpreting, and reporting of demonstration data;
- evaluating and reporting of technology performance; and
- developing the final report for the technology demonstration.

2.2.2 Developers

Responsibilities for the technology developers differed with the various technologies and are addressed separately in the following respective areas.

C Altair Equipment Company, Inc., was the developer of the ion-exchange unit using a nitrate-selective resin. This system was a procured item. Altair was responsible for:

- designing and constructing a resin-bed ion-exchange system capable of removing nitrates from mine wastewater;
- providing a system capable of removing nitrate concentrations of 10 to 40 mg/L at a flow rate of 5 to 20 gallons per minute (gpm) with a minimum of by-product waste;
- providing a system with the capability of resin regeneration;

- providing an automated system requiring a minimum of operational interface;
- providing delivery of the system per demonstration test plan schedule;
- providing operational startup support and training; and
- providing necessary documentation for operation and maintenance of the system.

C *SELENTEC* was the developer of the EIX unit. The EIX system was leased from Selentec. Selentec was responsible for:

- providing experimental methodology and design;
- operating a laboratory-scale EIX unit on simulated mine water and brine;
- designing and constructing an EIX system capable of removing 10 to 40 mg/L nitrate from mine wastewater at a flow rate of 5 to 10 gpm with a minimum of by-product waste;
- designing and constructing an EIX system capable of removing 300 to 1,000 mg/L nitrate from a chloride brine solution at a flow rate of 1 gpm with a minimum of by-product waste;
- providing a system with the capability of converting concentrated nitrates to nitrogen gas after removal from the process stream;
- delivering the system per the demonstration test plan schedule;
- assisting with data reduction and interpretation;

- providing operational support throughout the demonstration period;
- supplying necessary documentation for operation and maintenance of the system; and
- assisting with the completion of the demonstration final report.

C *Montana Tech of the University of Montana* (Montana Tech) was the developer of the biological denitrification reactor. This system was designed and constructed by Montana Tech with materials supplied by MSE. Montana Tech was responsible for:

- providing experimental methodology and design;
- operating a laboratory-scale biodenitrification unit using concentrated nitrate brine;
- designing and constructing a biological denitrification reactor capable of removing and destroying nitrate concentrations of 300 to 1,000 mg/L from a chloride brine solution at a flow rate of 1 to 5 gpm with a minimum of by-product waste;
- delivering the system per the demonstration test plan schedule;
- assisting with data reduction and interpretation;
- providing operational support throughout the demonstration period; and
- assisting with the completion of the demonstration final report.

Table 2-1. Demonstration Support Organizations.

Organization	Principal Contact	Telephone Number
U.S. Environmental Protection Agency	Thomas Powers	(513) 569-7550
U.S. Department of Energy (WETO)	Mel Shupe	(406) 494-7205
MSE Technology Applications, Inc.	Randy Hiebert	(406) 494-7233
TVX Gold Co. Mineral Hill Mine	John Hoak	(406) 848-7421
MSE-HKM, Inc., Analytical Laboratory	Kevin Kissell	(406) 494-1502

Table 2-2. Participating Developers.

Developer	Principal Contact	Telephone Number
Altair Equipment Co., Inc.	John Pinkowski	(215) 343-3120
Selective Environmental Technologies, Inc.	Michael Dunn	(770) 640-7059
Montana Tech of the University of Montana	Robert Mueller	(406) 496-4649

3. Predemonstration Activities

Several preliminary activities were required by MSE and the technology developers before the demonstration could be conducted. These activities included: 1) survey questionnaire completion; 2) technology selection; 3) site selection; 4) regulatory document preparation; and 5) analytical laboratory selection.

3.1 Survey Questionnaire

In an effort to ensure the MWTP funding was directed towards current mine waste problems, a questionnaire was sent by MSE to several mining operations concerning the major waste problems they were encountering. Ten out of 11 responses from the mining companies indicated removing nitrates was a significant problem. The survey also indicated that only five of these companies were presently treating for nitrates, probably due to unfavorable economics. Based on the findings of the survey, MSE promoted the Nitrate Removal and Destruction Project to help advance the development of innovative nitrate removal/destruction technologies.

3.2 Technology Selection

An extensive search was undertaken by MSE to evaluate innovative technologies that could be applied to the nitrate problem. Screening criteria used for selection were capital cost, operating and maintenance (O&M) cost, functionality, reliability, by-products generated, innovation, and development status. Of the 20 technologies that were screened, the following 3 showed the most promise in making nitrate removal more cost effective and environmentally responsible:

- C conventional ion exchange with nitrate-selective resin;
- C biological denitrification; and
- C EIX.

Since the three listed technologies ranked very

closely under quantitative screening methods, all three were chosen for testing. MSE's search indicated that the best solution to the nitrate problem in industry may be a combination of technologies rather than an individual one.

Following competitive bids, the following organizations were selected to furnish the field demonstration equipment.

- C Conventional Ion Exchange—Altair Equipment Company, Inc., of Jamison, Pennsylvania;
- C Biological Denitrification—Dr. Robert Mueller of the Center for Biofilm Engineering at Montana State University (later affiliated with Montana Tech); and
- C Electrochemical Ion-Exchange—Bradtec-US, Inc., which later changed its name to Selentec of Atlanta, Georgia.

3.3 Site Selection

Removing nitrates from mine wastewater is a continuous problem for many mining operations. Concerns over strict federal and state regulations and an interest in a cost-effective removal technology prompted the interest of several mining companies in this demonstration. Potential mine sites were evaluated using the following criteria:

- degree of characterization of the nitrate-contaminated effluent;
- accessibility, both legal and physical; and
- applicability of the selected technology.

The TVX Mineral Hill Mine at Jardine, Montana, met all of the above criteria. In addition, mine personnel enthusiastically supported the development of innovative technologies and also expressed a strong interest in a cost-effective nitrate treatment technology. Effluent from one of their historic portals contained 5 to 40 mg/L nitrate-

nitrogen at flow rates between 20 and 30 gpm. Mineral Hill personnel's willingness to assist the MWTP with this demonstration was a primary factor in choosing the Mineral Hill Mine for this demonstration.

An access agreement with the Mineral Hill Mine owner and operator, TVX Gold, Inc., was obtained prior to installation and operation of the project equipment. Discharge of treated water from the demonstration site was covered under existing State of Montana discharge permits. Permits for the construction of the building were under the jurisdiction of the Mine Safety and Health Administration (MSHA). An electrical permit was obtained from the State of Montana.

3.4 Regulatory Plans and Classifications

The following paragraphs briefly describe the required regulatory documents for this project.

3.4.1 DOE NEPA Categorical Exclusion

The environmental effects of the project were formally documented and reviewed in accordance with the DOE's procedures for implementing the National Environmental Policy Act (NEPA). Based on this review, it was determined this project was within the class of actions that do not individually or cumulatively have a significant effect on the human environment. The project was categorically excluded from further review under Section B3.1 of 10 Code of Federal Regulations (CFR) Part 1021, Subpart D, Appendix B. The document as it was submitted and the NEPA determination is included as Appendix A to this report.

3.4.2 Hazards Classification

A hazards analysis of the activities associated with the Nitrate Removal and Destruction Demonstration was conducted. This analysis found that the hazards associated with the work identified for this project were of the type routinely encountered and accepted by the general public

and as such were excluded from the requirements of the Safety Analysis and Review system as defined in DOE Order 5418.1B. All activities of this project were accomplished in accordance with all local, state, and federal environmental regulations; the MSE Risk Management manual (Ref. 3); Mineral Hill Mine directives; MSHA applicable regulations; and practices defined in the project health and safety plan. The project was assigned a Low Risk Hazard Classification.

3.4.3 Health and Safety Plan

A health and safety plan specific to this project was developed to establish the procedures and requirements that were used to minimize health and safety risks to persons working at a demonstration site (Ref. 4). The plan detailed responsibilities, personnel training, medical surveillance, site work practices, hazard evaluation, personal protection equipment, decontamination, and an emergency response plan. In addition to this health and safety plan, activities were conducted in accordance with applicable regulations of MSHA, Occupational Safety and Health Administration (OSHA), the MSE Risk Management Manual, and applicable Mineral Hill Mine policies.

3.5 Quality Assurance Project Plan

A QAPP was developed for this project and submitted to the EPA's Office of Research and Development for review and approval (Ref. 1). The QAPP was prepared by the MSE Quality Assurance Department against the standards provided in *Preparation Aids for the Development of QA Project Plans*, EPA/600/8-91/003 through 006, February 1991 (Ref. 5). Additionally, it served as a Standard Operating Procedure (SOP) document for the sampling team, the sample preparation team, the analytical team, and the data reduction team.

3.6 Demonstration Field Test Plan

In addition to the procedures and guidelines of the

QAPP, a detailed field test plan was created for the operation of the demonstration (Ref. 2). The plan outlined specific procedures for each of the technology demonstrations. Included were measuring and sampling procedures that included data recordkeeping, logbook entries, sampling procedures, sample handling and custody, and data quality control procedures. Additionally, the plan established expected operational parameters for each of the technologies, providing operation personnel with a baseline for operating temperatures, flow rates, process chemistry, etc. The plan also included the demonstration schedule that coordinated the arrival of equipment, startup and checkout of equipment, conditioning of systems, and QA verification.

3.7 Analytical Laboratory

The selection of the analytical laboratory to process the demonstration QA samples was based on laboratory qualifications and overall cost. The MSE-HKM, Inc., laboratory in Butte, Montana, was determined to have the capability to analyze all required samples and to be capable of providing timely service needed to meet the demonstration schedule. Also, the MSE-HKM laboratory is conveniently located near the MSE administration building where the majority of the support work was performed. Samples were transported from the mine site to the lab at least once a week to ensure the samples arrived prior to expiration of the holding time.

4. Demonstration Site Description

The Mineral Hill Mine is an operating gold mine located in Park County, Montana, near the town of Jardine, 5 miles from the community of Gardiner, Montana. To the south of the mine property lies the northern boundary of Yellowstone National Park, and to the north lies the Absaroka Beartooth Wilderness area situated within the Gallatin National Forest. This general area is also a wildlife wintering range for elk, deer, antelope, and bison (see Figure 4-1). Due to its fragile environmental location, the mine is continuously under the scrutiny of local, state, and federal environmental agencies. A continual environmental control and monitoring program is strictly enforced by TVX Gold, Inc., the owner and operator of the mine.

4.1 Mineral Hill Mining Operation

The history of the Mineral Hill Mine dates back to the 1880s with placer discoveries in the area as early as 1866. During the years that followed the initial opening, the mine closed and reopened many times. In the 1920s, the Mineral Hill Mine was producing arsenic as well as gold and silver. The demand for arsenic was caused by the boll-weevil blight that infected much of the southern United States at that time. The mine closed in 1958 and remained inactive until it was reopened in August 1989 through a joint venture between TVX Gold, Inc., and Homestake Mining, Inc. The mine is an underground operating that produces gold and some silver. The hard rock ore is trucked to the gold processing plant that has crushing and vat leaching facilities capable of treating 450 short tons of gold ore per day.

The mining operation takes place on the side of a 7,500-foot mountain with the westerly slope of the mountain bordering the Bear Creek drainage. The slope is spotted with evergreen trees and native grasses. In relation to the demonstration project area, Bear Creek lies approximately 150 feet to the

west and 30 feet below the site. The mine office building and core sample buildings are located within this general area (see Figure 4-2). One of the two small holding ponds near the demonstration site was used to contain treated water discharged from the ion-exchange unit. Discharges from the biodenitrification and EIX units were trucked to larger holding ponds on the mine site.

4.2 Site Characteristics

The old original mine portal at the 1,300-foot level collapsed and has filled the opening with several tons of rock. From this collapsed portal, a stream of water flows from the original underground drifts. This effluent stream varies seasonally in flow rate from 22 to 70 gpm (see Figure 4-3). A few feet below the portal, the water is collected in a small cistern with the overflow piped to a holding pond (see Figure 4-4). A second 2-inch pipeline was added to the cistern to supply water for this project. The level of nitrate in this water was discovered to vary significantly with the flow rate coming out the portal. A typical analysis of the portal water is shown in Table 4-1.

A pole-frame building with concrete flooring was constructed near the core sample storage area. This 30- by 40-foot building housed the demonstration equipment and all the necessary support equipment (see Figure 4-5). Mine effluent water was piped from the cistern approximately 130 feet above the building site and brought into the building at a head pressure of approximately 55 pounds per square inch (psi). A pump and piping arrangement in the building distributed the process waters to each of the demonstrated technologies. Treated process water was discharged to an existing percolation pond located near the demonstration building.

Table 4-1. Typical analysis of 1,300-level portal effluent.

Test Parameter	Value
Sample date	9/28/93
Flow rate (gpm)	29.0 gpm
pH	7.67
Temperature	6.0 °C
Total dissolved solids	609 mg/L
Total suspended solids	5 mg/L
Alkalinity, total	136 mg/L as CaCO ₃
Alkalinity, bicarbonate	136 mg/L as CaCO ₃
Alkalinity, carbonate	0 mg/L as CaCO ₃
Chloride	17 mg/L
Cyanide, total	<0.005 mg/L
Fluoride	<0.5 mg/L
Ammonia-N	0.05 mg/L
Nitrate-N	14.2 mg/L
Nitrite-N	<0.05 mg/L
Ortho phosphate	0.11 mg/L
Sulfate	179 mg/L
Calcium	115 mg/L
Magnesium	30.3 mg/L
Potassium	10.6 mg/L
Sodium	12.6 mg/L
Arsenic	0.60 mg/L

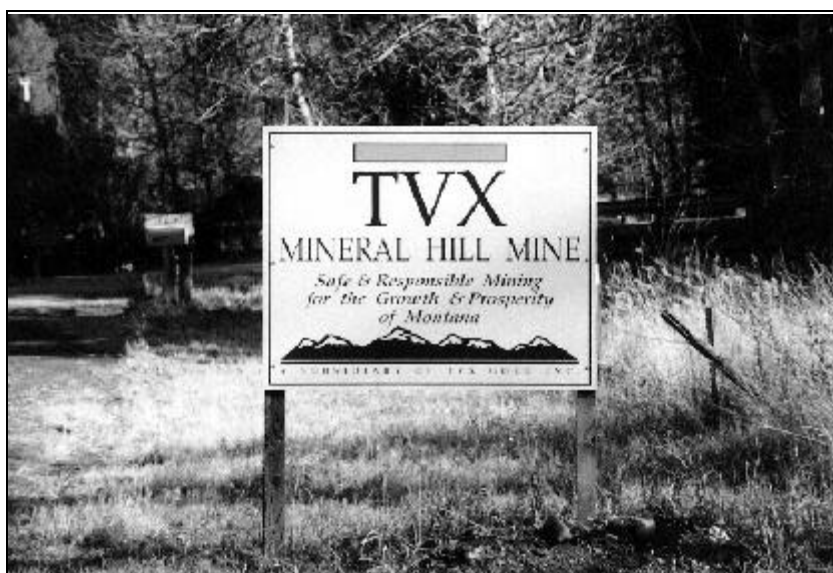


Figure 4-1. Mineral Hill Mine.



Figure 4-2. Process building.



Figure 4-3. Original mine portal.



Figure 4-4. Portal cistern.

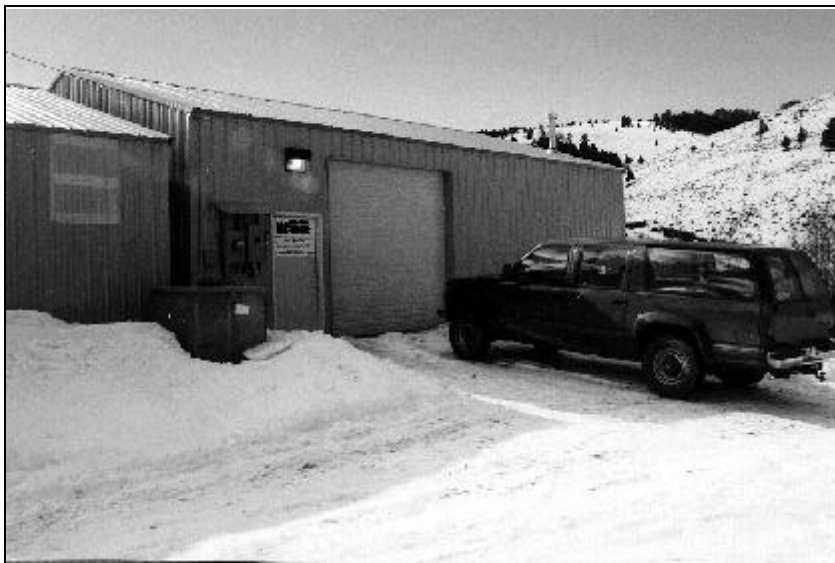


Figure 4-5. Demonstration building.

5. Demonstration Technology Description

This demonstration was designed to use a combination of technologies assembled in a configuration to remove nitrates from mine wastewater. Figure 5-1 illustrates the schematic layout of the demonstration, showing the flexibility of the system to use the technologies in combination or in a stand-alone treatment configuration. In addition to the equipment shown in the figure, an existing biological reactor was tested. This reactor was located in a nearby building (Rainbow Room) and was actively treating raw mine water by removing and destroying nitrates prior to the start of this project. The following is a list of technology configurations as they were demonstrated.

- C Ion exchange using a nitrate selective resin.
- C Electrochemical ion exchange treating raw mine water.
- C Electrochemical ion exchange treating a brine solution containing concentrated nitrates from the ion-exchange process.
- C Biological Fixed Film Reactor (FFR) treating raw mine water (Rainbow Room).
- C Biological FFR treating a brine solution containing concentrated nitrates from the ion-exchange process.

5.1 Ion Exchange Using Nitrate-Selective Resins

Ion exchange is a well-developed technology whereby a liquid medium exchanges an ionic species with a solid medium when the two come into contact. It is a sorption process in which a solid phase (typically a resin) contains bound groups that carry an ionic charge in conjunction with free ions of the opposite charge that can be displaced. The process is a reversible reaction involving chemically equivalent quantities. In the case of nitrate removal, chloride ions attached to the resin are displaced by nitrate ions in solution. When the active sites of the resin become filled

with nitrate ions, regeneration with a concentrated chloride solution is required, returning the resin to its initial condition.

A nitrate-selective resin, Purolite A-520E, was chosen for this project. Use of a selective resin improves the efficiency of the resin bed and reduces operating costs. Nitrate selectivity is not an absolute however, it simply means the resin has a higher affinity for nitrate than it does for equal concentrations of most other anions. When present in sufficiently high concentrations, anions such as chloride and sulfate are readily adsorbed by the resin.

The need to improve the operation of downstream equipment is another reason for using a nitrate-selective resin. For example, the sulfate anion is a strong competitor with nitrate for an anion-exchange site. If the regeneration stream is to be sent to a technology using membranes, sulfates can combine with calcium to form calcium sulfate scale that is acid insoluble and is difficult to remove from the membrane.

A basic block diagram showing the flow streams of the system demonstrated can be found in Figure 5-2 and photographs of the system in Figures 5-3 and 5-4.

5.1.1 Developer's Performance Claims

Altair, Inc., supplied the ion-exchange equipment. Ion exchange is a well-understood technology with numerous equipment manufacturers. The Altair equipment was designed to run automatically with very little operator attention, except for preparation of the brine regenerant solution.

The nitrate-selective ion-exchange resin was type A-520E supplied by Purolite, Inc., and is a strong-base anion resin specially designed for the removal of nitrates from water for potable

processes. This resin was chosen for its high affinity for nitrate even in the presence of moderate to high concentrations of sulfate.

5.1.2 General Operating Procedures

The ion-exchange system is operated in a batch mode that is fully automated by a Programmable Logic Controller (PLC). Table 5-1 shows the sequence of steps for each batch including the flow rates and duration of each step. Operator adjustments to the process flow or program changes to the PLC timing are easily made. The batch process is initiated by pushing a button on the local control panel. For this demonstration, the unit was programmed to stop at the completion of each batch. The programmed stop can be removed, allowing the system to automatically start the regeneration cycle and then start a new batch.

The support systems for the ion-exchange unit consisted of a sodium chloride regeneration system, treated water temporary storage tank, and concentrated nitrate brine storage tanks. The sodium chloride regenerant solution was prepared in a 100-gallon tank and then transferred to a 1,600-gallon tank. Once in the larger tank, the concentrate was diluted to bring the brine solution to the proper density. The water used for diluting the solution was the treated effluent water (nitrates removed) from the ion-exchange unit.

The treated effluent from the unit was temporarily stored in a 1,600-gallon tank. This water was analyzed on site for nitrates and chloride and then discharged to the percolation pond if the water quality was acceptable. During resin regeneration, the brine solution containing the concentrated nitrate solution was sent to storage vessels with a total capacity of 4,000 gallons.

5.1.3 Technology Advantages

Ion exchange is a well-developed technology and is a widely used process for nitrate removal. Ion-exchange units can be purchased off the shelf and

require little maintenance. The technology was chosen for its effectiveness, simplicity, and relatively low cost of operation. The highly selective anion resin also allows the process to be adapted to various different operating conditions with successful results.

5.1.4 Technology Limitations

Although ion exchange is proven and effective, it does have several important drawbacks. Disposal of the waste brine produced during regeneration of the ion-selective resin is the most important of these. This brine contains high levels of nitrate as well as excess sodium chloride from the regeneration step. This brine solution is a problem and requires treatment and/or disposal. An added treatment step can greatly increase the cost and complexity of the overall process.

Another problem with ion exchange is fouling of the resin bed. Fouling reduces the efficiency of the process by decreasing the number of reaction sites available for nitrate removal. Fouling also increases chloride levels in the effluent and can cause more frequent replacement of the resin.

5.1.5 Equipment and Accessories

The ion-exchange equipment was mounted on a single platform skid with an overall measurement of 6 feet wide by 3 feet deep and 8 feet high and occupied about 18 square feet of floor space. The unit weighed 1,200 pounds prior to adding resin or water.

Ion-Exchange System General Specifications

Number of units	2 each, A&B
Vessel size	24 x 72 inches
Design pressure	100 psi, ASME Code
Test pressure	150 psi
Tank lining	epoxy
Resin volume	20 cubic feet total
Resin type	Purolite A-520E
Exchange capacity, wet	13 kilograms

Totalizing flow meter Great Lakes Model
672F

The following is a list of equipment that was necessary to support the ion-exchange system operation:

Support Equipment

Regenerant preparation tank	100 gal fiberglass
Regenerant storage tank	1,650 gal polyethylene
Concentrated nitrate storage tank (large)	2,550 gal polyethylene
Concentrated nitrate storage tank (small)	1,650 gal polyethylene
Processed water storage	1,650 gal polyethylene
Pumps	3 each, single phase, 115 V ac
Air compressor (for valve operation)	3 hp, 115 V ac
PVC pipe and valves	1 inch and ½ inch
Equipment power	115 V ac, single phase, 4 amp

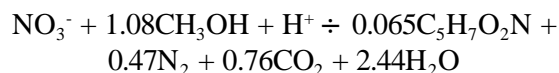
5.2 Biological Denitrification

Biological denitrification (or biodenitrification) consists of the reduction of nitrate ions to nitrogen gas using heterotrophic organisms under anoxic (low oxygen) conditions. Heterotrophic organisms, which represent the majority of microorganisms, are those that use organic carbon as both carbon and energy sources. The reaction takes place in the presence of an external carbon source such as methanol, ethanol, or acetic acid. In this case, methanol was selected as the nutrient for the demonstration. The nutrient acts as the electron donor to reduce the nitrate, the electron acceptor, to nitrogen gas. The biological reaction is facilitated by environmental conditions favorable to microbial growth such as the optimum temperature, pH, and the presence of other micronutrients and trace elements, such as phosphate. A mixed population of bacteria, indigenous to the Mineral Hill Mine

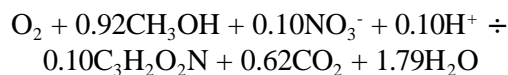
water, was used for the demonstration. Although the indigenous bacteria will slowly destroy nitrate in their native environment, placing them in bioreactors at a high density gives them optimum growing conditions so nitrate can be destroyed rapidly.

In addition to removing nitrate from the raw mine water, the biological denitrification process was used to destroy nitrates in a concentrated brine solution, which was a product of the ion-exchange process. This process combination was used because it has advantages over either ion exchange or biological denitrification alone. The greatest advantage is that the concentrated nitrate wastestream is eliminated. Also, the risk of contaminating the treated water with organic compounds from the denitrification process is greatly reduced. A bioreactor system capable of processing concentrated nitrate brine was designed and constructed by Montana Tech.

The chemical reaction that takes place in the anoxic reactors is shown below. Methanol is the nutrient, and $C_5H_7O_2N$ is an empirical formula for typical biomass.



The chemical reaction that takes place in the aerobic reactors is shown below:



A basic block flow diagram is shown in Figure 5-5, and the system as demonstrated is shown in Figure 5-6.

Many pilot-scale and a few full-scale biological denitrification plants have been built for municipal applications, particularly in Europe. Mineral Hill Mine in conjunction with Dr. Robert Mueller of

Montana Tech (formerly affiliated with Montana State University's Center for Biofilm Engineering) has a pilot-scale system in operation at the mine site. This bioreactor processes the raw mine water as it comes from the portal. With approval from Mineral Hill, this system was also evaluated as part of the demonstration (see Figure 5-7).

5.2.1 Developer's Performance Claims

The biological denitrification unit developed at Montana Tech was designed to treat regenerant brine from the ion-exchange unit. The system developed was made up of eight anoxic reactors and two aerobic reactors with volumes of 0.15 cubic meters (m³) each. The goal was to design a biological treatment system that could treat brine containing nitrate concentrations of 300 to 1,000 mg/L NO₃-N at a rate of 0.25 gpm. The hydraulic residence time for the system was 26 hours.

5.2.2 General Operating Procedures

The following discussion is applicable to the reactor system constructed specifically for this project to process concentrated nitrate brine and to the existing biodenitrification unit that treated raw mine water. The piping and valve arrangements on the reactors allowed the process flow to be routed through the reactors in series, in parallel, or in any combination thereof.

Initial conditioning of the bioreactor was accomplished by filling the system with raw mine water and establishing a continuous low flow rate. A prepared biomass inoculum was injected into the inlet process flow stream and permitted to circulate through the entire system. Methanol (a nutrient source) was then introduced to establish a working biomass after several days. The amount of brine in the feed was gradually increased until the reactor was fully operational on 100% brine. This conditioning process was controlled by measuring the nitrate level in the effluent and modifying the rates based on this data.

After the system was conditioned on the nitrate brine, adjustments to the process flow rate were made to optimize performance. Other than daily checks on process and nutrient flow rates, there were no other operational requirements.

5.2.3 Technology Advantages

Biological denitrification is a simple process and requires little maintenance once the biomass is established. One advantage biological denitrification has over conventional ion exchange is the continuous nature of the process. By running continuously, the speed and efficiency of the process is improved. Another major advantage with biodenitrification is that the need for a regeneration step is eliminated and the amount of waste generated is significantly reduced. Another advantage to biodenitrification is that additional anions (such as the chloride) are not added to the effluent water.

5.2.4 Technology Limitations

Biological denitrification, although promising, is not without its limitations. Among these is the need for continuous addition of nutrient to sustain bacterial growth. Nutrients such as ethanol or methanol are relatively inexpensive but still add to the overall cost of the treatment process. The bacteria are also susceptible to poisoning by undesirable constituents that may be in the water. Biological systems work best when conditions are constant. Due to long growth times, response times can be slow when responding to large or rapid variations in operating parameters.

Posttreatment of the effluent water may also be required to remove constituents such as excess biomass or excess nutrient in order to meet drinking water standards. These posttreatment techniques, such as filtration or chlorination, can add to the overall cost and complexity of the process.

5.2.5 Equipment and Accessories

The biological reactor cylinders were mounted along the wall of the demonstration building with the piping, valves, and flow meters mounted between cylinders. This provided a means of support for the cylinders and allowed access to valves and flow meters. The system occupied a floor space of approximately 36 square feet (ft²).

Biodenitrification Fixed Film Reactor

Number of anoxic reactors	8 each
Number of aerobic reactors	2 each
Reactor size	12 inches diameter by 80 inches long
Reactor volume	Total 160 cubic feet (ft ³)
Reactor material	Polyvinyl chloride (PVC)
Reactor substrate	Biomedia (proprietary)
Methanol metering pump	1 each
Process supply pump	1 each
Air purge flow meters	2 each
Process totalizing flow meter	1 each
Balancing flow meters	10 each
Piping and valves	PVC
Offgas purge valves	2 each

Following is a list of equipment that was necessary to support the biological reactor system:

Support Equipment and Consumables

Concentrated nitrate storage tank (large)	2,550 gal polyethylene
Concentrated nitrate storage tank (small)	1,650 gal polyethylene
Effluent brine storage tank	1,650 gal polyethylene
Air compressor	Aerobic purge
Methanol	1 gal per 24 hrs
Interface pipe and valve	PVC
Equipment power	120 V ac, single phase, 5 amp

5.3 Electrochemical Ion Exchange

Electrochemical ion exchange technology uses a combination of ion exchange and electrodialysis to remove nitrates from wastewater and to eliminate the production of waste by-products associated with conventional ion exchange. A basic block flow diagram is shown in Figure 5-8, and the system as demonstrated is shown in Figures 5-9 and 5-10.

Ion exchange is used in a conventional manner to concentrate the nitrates in a nitrate-selective resin arranged in columns in each EIX resin cell. From the resin, the nitrate ions are forced to migrate through a selective membrane by a direct current electrical field imposed across the resin bed. Current is carried by the migration of anions passing from the cathode (catholyte) solution compartment across the membrane, through the resin compartment, across another membrane, and into the anode solution (anolyte) compartment. During this process, the nitrate ions are transferred from the resin to the anode solution. The anode solution with the concentrated nitrates is then circulated through the destruction cell where the nitrate is electrochemically converted to gaseous nitrogen. The destruction cell consists of a series of sequential cathode and anode plates energized with a direct current power supply.

Electrochemical ion-exchange employs bicarbonate (HCO_3^-) ions as the continuous ion-exchange resin regenerant. The bicarbonate ions migrate from the catholyte solution across an anion-selective membrane into the resin compartment. Bicarbonate ion concentration is maintained by bubbling carbon dioxide gas through the catholyte, producing HCO_3^- ions.

On passing through the resin compartment, bicarbonate ions displace nitrate ions on the resin's anion-exchange sites. The nitrate ions then migrate across another anion-selective membrane into the anolyte compartment. As nitrate concentration builds up in the anolyte loop, a

portion of the anolyte is diverted to the destruction loop. Finally, the nitrate-laden solution is circulated through the destruction cell.

5.3.1 Developer's Performance Claims

Electrochemical ion exchange is an innovative technology developed by Selentec for the destruction of nitrates from wastewater. The process has been tested at the pilot-scale level by Selentec and has produced encouraging results. The process is flexible with regard to the nitrate feed concentrations and can be used to treat both dilute concentrations and very high concentrations like those found in ion-exchange regenerant solutions. The process is claimed to not be sensitive to pH or other constituents in the water since the resin is nitrate-specific.

Maintenance of the units operated by Selentec to date has not proven to be a problem. Similarly, Selentec has seen no degradation of the resin, although they expect the resin will need to be changed annually during continued operation. To date, EIX has not had any problem with scale on the membranes, which is a common problem with electrodialysis units. Selentec personnel indicated that previous test runs did not investigate resistance to biological fouling; however, they did not expect that to be a problem with mine effluent.

5.3.2 General Operating Procedures

The EIX system was prepared for demonstration by first filling the anode and cathode reservoirs with the anolyte and catholyte solutions. Mine water or brine was then introduced to the resin bed chambers while allowing the anode and cathode chambers to fill with the electrolytes. This was followed by establishing pump flow rates for the electrolytes and the process mine water. These flow rates were adjusted to balance pressures across the membranes to mitigate cross contamination of electrolytes and mine waters. By using either raw mine water or the concentrated nitrate brine as the process stream, the system was first permitted to load the resin with the nitrate

ions. This resin-loading procedure was monitored by field analyzing samples of the effluent process with a nitrate-selective ion probe.

When sample analysis indicated an increased nitrate level in the effluent, indicating resin saturation, the process stream was stopped, and demineralized water was recirculated through the resin to provide cooling.

Resin regeneration and nitrate destruction were then initiated. The regeneration cycle was started by recirculating the anolyte, catholyte, and resin compartment cooling water, then establishing electric current flow from cathode to anode through the EIX cells. An increase in voltage (corresponding to an increase in cell resistance) on the constant-current power supply indicated resin regeneration was nearly complete.

The nitrate destruction cycle was started by recirculating the nitrate-laden destruction loop solution (initially filled with a strong sodium hydroxide solution) through the destruction cell, then energizing the cell power supply. Nitrate destruction was monitored by analyzing destruction cell inlet and outlet nitrate concentrations. The collection, regeneration, and destruction procedure was repeated throughout the demonstration period.

Switching between the resin loading and the regeneration/destruction modes along with periodic sample analysis were the operational requirements for the system. Flow balancing to maintain equal pressure across the membranes was also required, usually once per batch cycle.

5.3.3 Technology Advantages

Electrochemical ion exchange has several important advantages over using either ion exchange or electrodialysis alone. It combines the selectivity and effectiveness of ion exchange with the nitrate destruction capabilities of electrodialysis. Conventional ion exchange merely concentrates the contaminant during the

regeneration step and produces regenerant brine solutions containing high concentrations of nitrates that must be disposed. By using electrodialysis, no concentrated wastestreams are produced.

Also, by combining the two technologies, the process can run continuously, with only infrequent observation by an operator. By running continuously, both the speed and efficiency of nitrate removal are increased.

5.3.4 Technology Limitations

Problems encountered with EIX can include scaling of the selective membrane, fouling of the anion-selective resin, and the cost of power consumption associated with its operation. Because the technology uses ion exchange as an initial step, it is susceptible to the same problems with resin fouling and degradation. However, the cost of power consumption is offset by eliminating the need for additional waste disposal. One other limitation is the relative complexity of the technology as compared with other removal technologies.

5.3.5 Equipment and Accessories

The EIX system was constructed within a steel frame that housed all components with the exception of the power supplies for the resin bed separation units and the destruction cell and a stepdown 480-/220-volt transformer. Circulation pumps were mounted near the bottom of the system and electrolyte reservoirs near the top. There were two resin bed separation units that were mounted on opposite sides of the centrally mounted control panel. The destruction cell was located on top of the structure along with offgas boxes that vented the electrolyte reservoirs and destruction cell of gases. The system occupied approximately 42 square feet of floor space and weighed approximately 2,200 pounds.

Electrochemical Ion Exchange System

Resin bed separation units	2 each
Resin volume	0.8 ft ³ per unit
Destruction cell	1 each
Operating volume	1.2 ft ³
Flow meter	0.5-16 gpm
Flow indicator	8 each
pH meter	2 each
Temperature indicator	2 each, switchable
	4 each
Pressure gauge	16 each
Electrolyte reservoirs	2 each, 7 gal each
Destruction loop reservoir	3 gal
Pumps, mag-coupled	4 each
Transformer	480 to 220 stepdown
	1.5 kilovolt amps
	(kVA)
Power supply	2 each, 0-70 V dc

Following is a list of equipment that was used to support the EIX system:

Support Equipment and Consumables

Concentrated nitrate storage tank (large)	2,550 gal polyethylene
Concentrated nitrate storage tank (small)	1,650 gal polyethylene
Effluent brine storage tank	1,650 gal polyethylene
Process supply pump	1 each
Process filters	2 each (5 micron)
Gaseous nitrogen	Destruction cell purge
Gaseous carbon dioxide	Catholyte purge
Gas flow indicators and regulators	2 each
Interface pipe and valve	PVC
equipment power	480 V ac, 3 phase, 40 amp

Table 5-1. Control sequence.

Unit A	Flow Rate (gpm)		Unit B	Flow Rate (gpm)		Time
	Upflow	Downflow		Upflow	Downflow	
Service	15	-----	Service	15	-----	22 hrs
Service	6	-----	Backwash	6	-----	10 min
Backwash	6	-----	Brine/Block	3	3	20 min
Brine recovery	6	3	Brine displace	3	3	30 min
Brine/Block	3	3	Idle	-----	-----	20 min
Brine displace	3	3	Idle	-----	-----	30 min
Fast rinse	10	-----	Fast rinse	10	-----	20 min

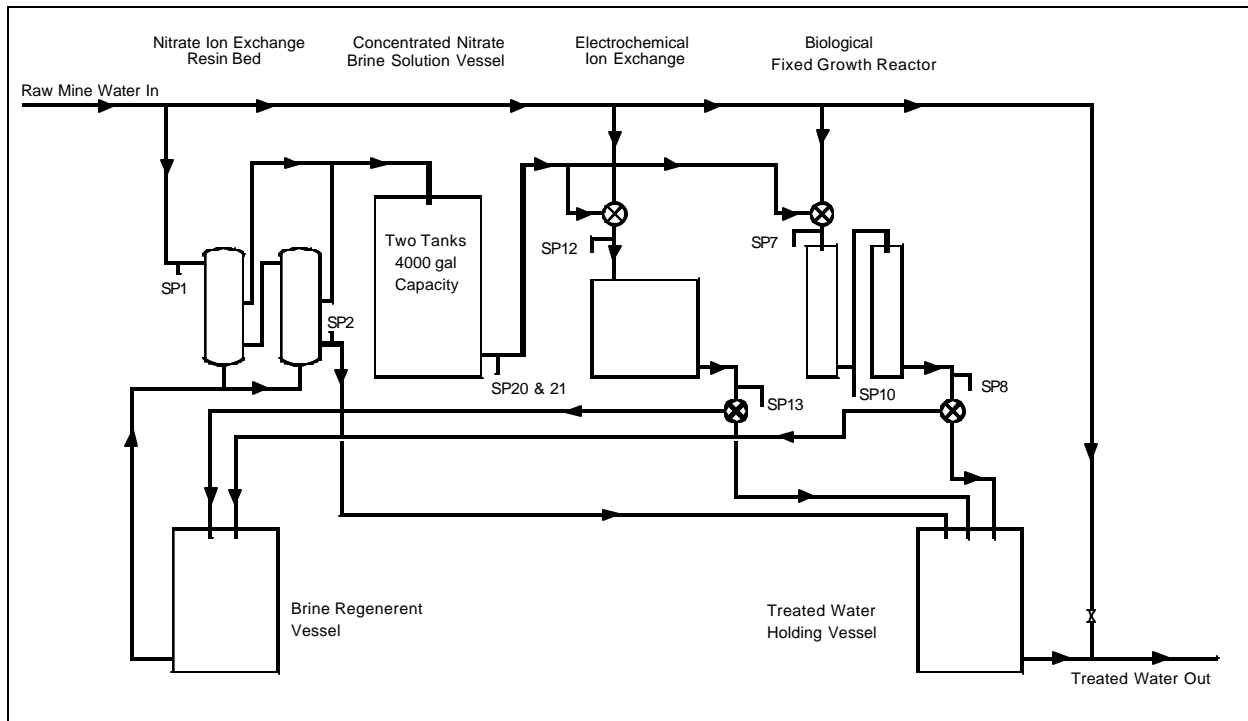


Figure 5-1. Nitrates removal and destruction demonstration block diagram.

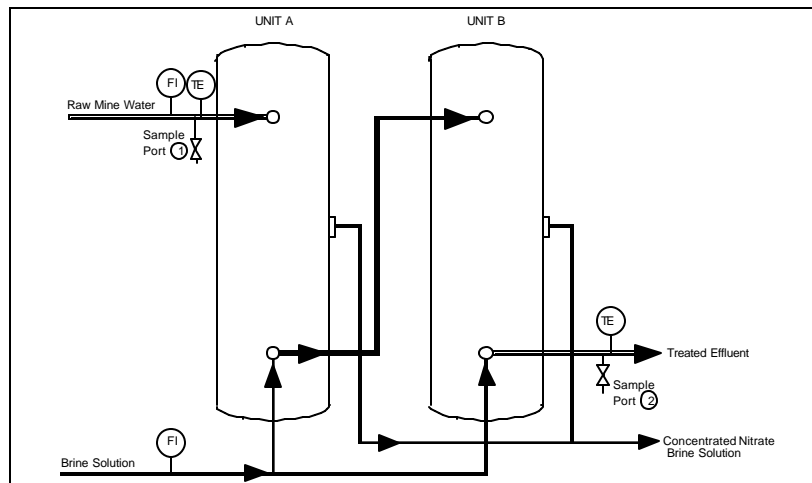


Figure 5-2. Ion-exchange system flow diagram.



Figure 5-3. Ion-exchange system.



Figure 5-4. Ion-exchange control panel.

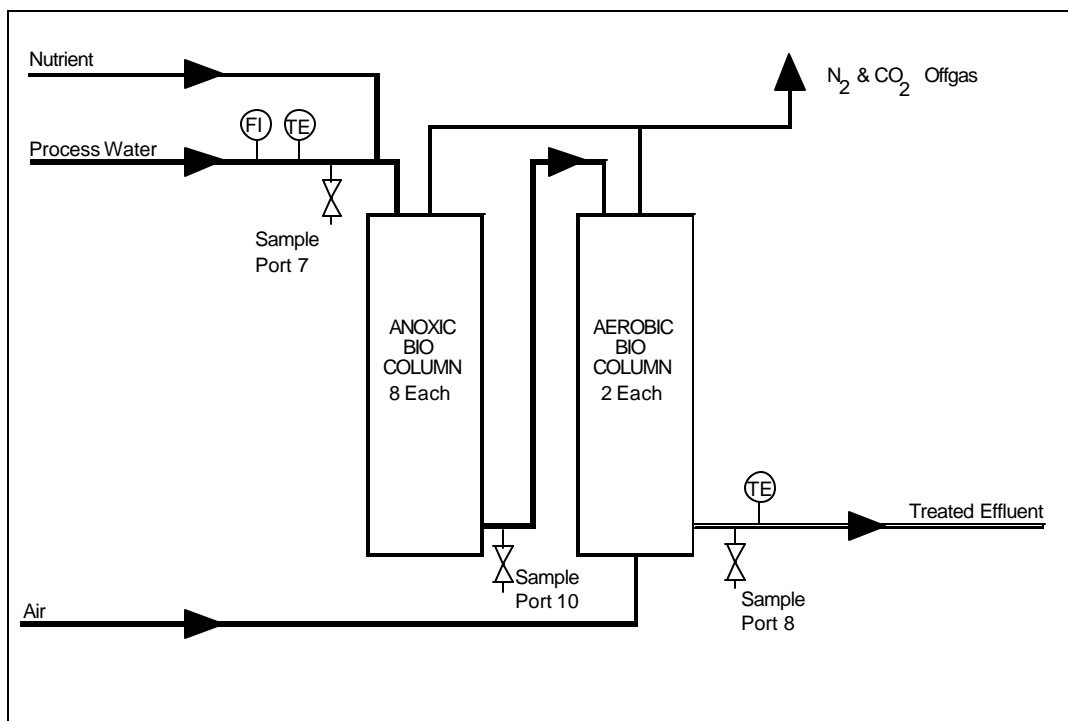


Figure 5-5. Biodenitrification FFR basic block flow diagram.



Figure 5-6. Bionitrification FFR (concentrated nitrate brine).



Figure 5-7. Bionitrification FFR (raw mine water).

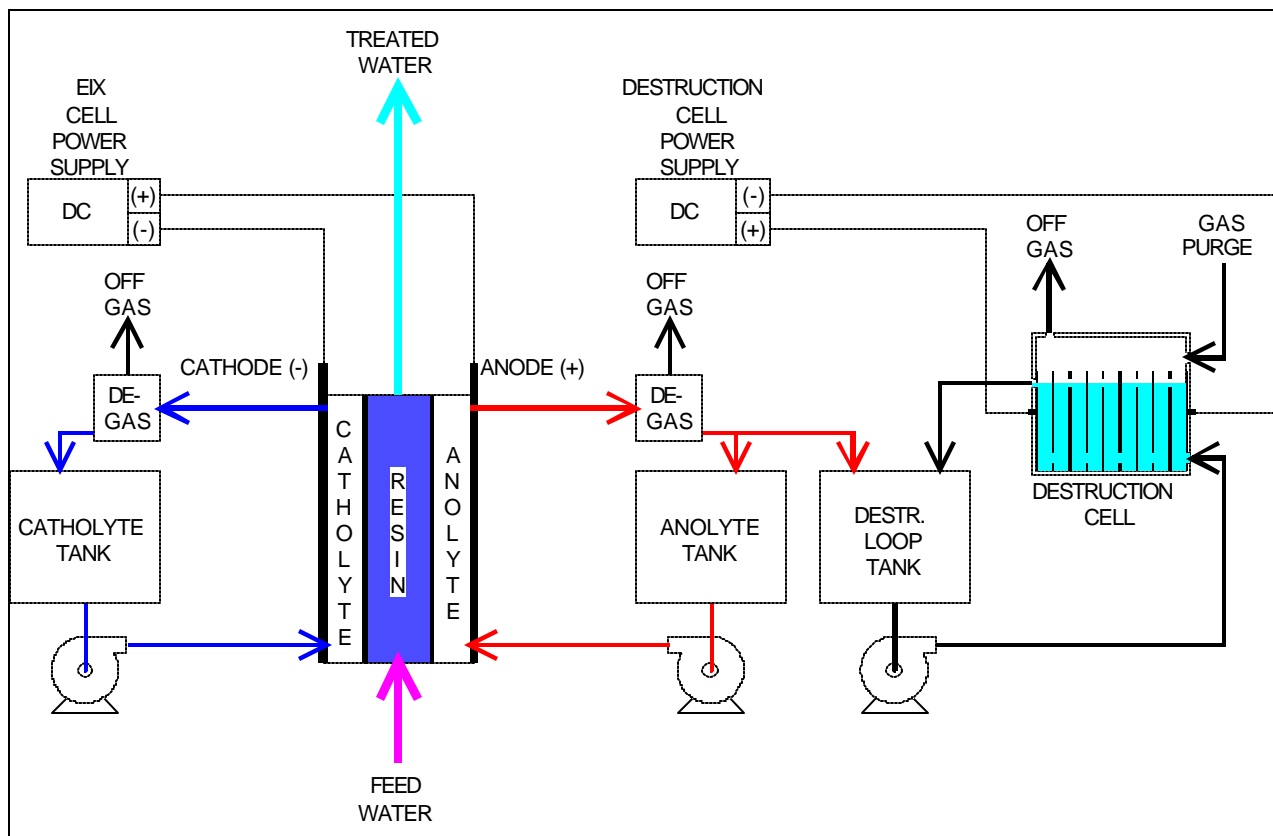


Figure 5-8. EIX basic block flow diagram.

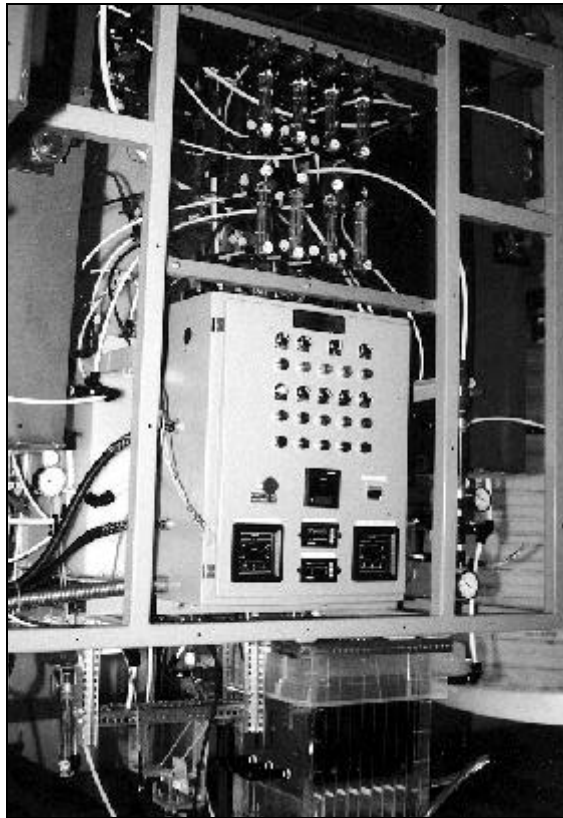


Figure 5-9. EIX control panel.

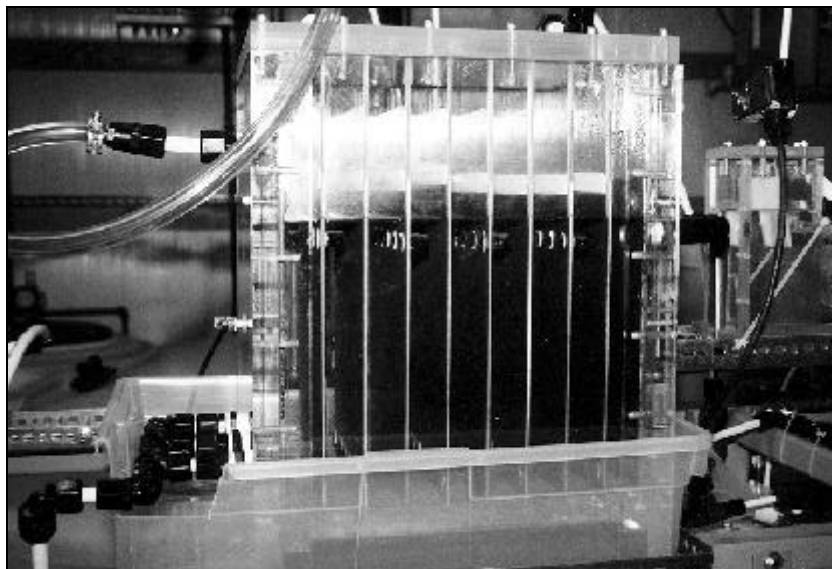


Figure 5-10. EIX destruction cell.

6. Experimental Design

6.1 Technology Demonstration Objectives

The objective of the demonstration was to illustrate the feasibility of combining several innovative technologies in a process train to effectively remove and destroy nitrates from a mine wastewater stream while minimizing or eliminating by-products. Technologies such as ion exchange, in its conventional form, and reverse osmosis are costly and generate concentrated nitrate waste by-products. The purpose of this demonstration was to evaluate technologies that are less costly and that destroy the nitrates, thus avoiding waste disposal problems.

6.2 Factors Considered

Several factors were considered during the development of the experimental design. Questions that needed to be answered to ensure a successful design were formatted and logical decisions derived. These questions are listed below.

- C How many demonstrations can be conducted simultaneously?
- C How long should each technology be demonstrated to ensure stable performance and identify trends?
- C What flow rates should be optimum?
- C At what location should samples be taken?
- C At what intervals should samples be taken?
- C What size should samples be?
- C Should sample intervals be changed with nitrate concentration?
- C Are the number of samples within the budget for lab analysis?
- C Can the number of samples be reduced without compromising data trends?
- C What type of sample analysis is required for each evaluation?
- C What data in addition to performance data is needed to track operational costs?

- C How can personnel changeout be coordinated with sample holding time?
- C Can the overall demonstration schedule be reduced without compromising the evaluation?
- C What is considered a waste by-product?
- C How will waste by-products be measured?

6.3 Sampling Design

Quality control (QC) sampling formats were designed for each of the technologies based on the demonstration test plan. Sample locations and time intervals between samples were established to aid in the identification of trends and to produce adequate data to evaluate the technology's overall performance. During the development stage of the sampling formats, close scrutiny was given to the balance between adequate sampling and oversampling. The type of lab analysis for each sample was established to ensure there was adequate data to identify interference effects.

Additional samples were included in each of the formats. These were field samples to be analyzed in the field and used to monitor the technology's day-to-day performance. The results of the analysis from these samples were recorded on the Demonstration Data Record forms. Noncritical temperature and pH measurements were also recorded on these forms.

The Data Record forms listed the quality assurance (QA) samples, field samples, preassigned QA lab sample numbers, day and time of each sample, sample location, type of sample (field or lab), sample preservative (if needed), duplicates, blanks, etc. See Section 7 for detailed information.

6.4 Statistical Analysis

Characterization of the measured performance of the demonstrated technologies was accomplished using descriptive statistical methods. In planning

the demonstration, the following factors were considered critical to the success of the demonstration. Other variables were monitored but were considered of lesser importance.

- ⌘ Nitrate removal
- ⌘ Operational cost
- ⌘ By-product waste minimization

Estimates of the mean and standard deviation assume a normal distribution. Confidence intervals assume two standard deviations; ($2s$) or 95% of the sampled data will fall within 95% of the true mean.

7. Field Sampling and Analysis

7.1 Techniques and Methods

All sampling, storing, and transporting was completed using MSE SOPs FI-1 and G-4 through G-8. Samples were taken by opening the prescribed sample port and flushing the piping and port for several seconds to ensure the sample was representative of the product. Sample bottles were high-density polyethylene (HDPE) provided by the MSE-HKM laboratory. The sample bottle was then rinsed three times with sample product, and the sample bottle was filled after the third rinse. Sample bottle lids and labels were secured and sealed with parafilm and cellophane tape.

Temperature and pH samples were taken after allowing product to flow for several seconds from the sample port to stabilize the temperature in piping and ensure fresh product. Sample bottle temperature was stabilized by filling a bottle three times with the sample product. Temperature was measured immediately after the third “rinse” using a hand-held mercury thermometer. Temperature samples were taken at the sample port at the time designated on the sample data form. pH was measured using an Accumet 1003 meter with a temperature compensating pH probe. The Accumet was calibrated daily, using up-to-date pH buffers, according to procedures outlined in the *Measurement Procedures Handbook* (Ref. 6).

Brine samples were taken from the brine storage tank in use and was continuously circulated to ensure a representative sample was taken. Electrochemical ion exchange brine test level measurements were not complicated by the addition of brine to the storage tanks from the resin bed nitrate ion-exchange unit (NIX).

Fixed film reactor - brine (FFR-B) and fixed film reactor - mine water (FFR-W) samples were taken as noted above with the exception of total organic carbon. Total organic carbon samples were taken using 8-ounce amber glass bottles with

H₂SO₄ as the preservative. These bottles were supplied by the MSE-HKM laboratory. Orthophosphate and acridine orange samples were taken at the weekly shift rotation to ensure prompt delivery to the laboratory.

The quantity of mine water processed by the NIX and EIX units was measured by a flow totalizer located on each unit. The amount of mine water processed by the FFR-W unit was measured by a flow totalizer located in the Rainbow Room. The amount of brine processed by the EIX and the FFR-B was measured using calibrated level indicators on the brine tanks and compared to in-line process flow totalizers.

7.2 Field Sample Analysis and Data Recording

In addition to the QC sampling for laboratory analysis, it was necessary to take samples for field analysis to ensure the technology was within its operational parameters. These field samples were analyzed with instruments and reagent test sets using EPA accepted methods and equipment manufacturer procedures. Results of these field analyses were recorded on the data record forms for each demonstrated technology test series. The forms served two basic purposes, a guide for operation and sampling personnel of where and when to take samples and a controlled method for recording results of the field data and analysis. Additionally, this form was used for recording process pH levels, process temperatures, and process flow rates. A sample of the data record form for the biodenitrification tests is shown in Figure 7-1, which is a copy of the first page of a prepared set of 28 covering the 4-week demonstration. Each form consisted of two pages. Page two provided space for recording model numbers, serial numbers, and National Institute of Standards and Testing (NIST) calibration due dates of equipment used for data collection. Buffers used for pH meter calibrations were also

recorded on this page. A sample of this page is shown in Figure 7-2.

7.3 Instrument Accuracy

The performance evaluation of the demonstrated technologies was, in part, a function of the instrument quality and its calibrated accuracy. Instruments installed for monitoring temperature, flow rate, tank level, and pressure were selected to obtain an overall accuracy capability of at least 1% of the full-scale span adjustment (unless otherwise indicated below). Calibration of these

instruments was accomplished before and at the conclusion of the demonstration. A calibration history card was initiated for each instrument showing its accuracy, five-point calibration data, date of calibration, and NIST traceability. A characterization and error analysis was performed to identify the mean and standard deviation for each instrument. This was used to develop a 95% confidence interval for each measurement. An outline of the calibration requirements as approved by the EPA in the QAPP is shown in Table 7-1.

Table 7-1. Calibration requirements for process field measurements.

Parameter	Measurement Classification	Process Instrument	Calibration Procedure	Frequency of Calibration	Expected Range/Acceptance Criteria
Total flow of raw mine water inlet to EIX (resin bed)	Critical	Volumetric flow rate with totalizer	Manufacturer's procedure using NIST traceable test equipment	3 months for flow instrument with scheduled verification of test equipment at INEEL Standards Lab ¹	10 gpm +/- 0.5 gpm
Tank levels concentrated nitrate brine solution	Critical	Volumetric tank levels Tank #1 & 2, differential pressure level transmitter with digital indicators	Manufacturer's procedure using NIST traceable test equipment	6 months for pressure transmitters with scheduled verification of test equipment at INEEL Standards Lab ¹	Tank level measurements 2,550 & 1,650 gal to within +/- 6.25 gal
NIX process temperature - inlet and outlet	Noncritical	Type T, 1/8", enclosed thermocouple, readings taken with NIST traceable test equipment, curve fit for type T TC	Element characterized to +/- 1 EC using lab standard and referenced to IPTS-68- microvolt tables	Certified to +/-1 EC, scheduled verification of test equipment at INEEL Standards Lab ¹	Inlet and outlet 0 - 50 EC +/- 1 EC
Raw mine water inlet flow rate to EIX system	Critical	Volumetric flow rate instrument	Calibrated using in-line 0.25% full- scale accuracy flow standard and read with NIST traceable test equipment	Before field test series scheduled verification of test equipment at INEEL Standards Lab ¹	Flow rate adjusted for optimum performance 3-6 gpm, accuracy +/- 0.5 gpm
Concentrated nitrate brine solution inlet flow rate to EIX system	Critical	Volumetric flow rate instrument, corrected for density	Calibrated using in-line 0.25% flow standard and read with NIST traceable test equipment	Before field test series, scheduled verification of test equipment at INEEL Standards Lab ¹	Flow rate adjusted for optimum performance 1-4 gpm, accuracy +/- 0.5 gpm
EIX process temperature - inlet and outlet.	Noncritical	Type T, 1/8", enclosed TC, readings taken with NIST traceable test equipment, curve fit for type T TC	Element characterized to +/- 1 EC using lab standard and referenced to IPTS-68- microvolt tables	Certified to +/-1 EC, scheduled verification of test equipment at INEEL Standards Lab ¹	Inlet 0 - 50 EC +/- 1 EC Outlet 20 - 100 EC, +/- 1 EC
Raw mine water inlet flow rate to biological (FFR) system	Critical	Volumetric flow rate instrument	Calibrated using in-line 0.25% flow standard and read with NIST traceable test equipment	Before field test series scheduled verification of test equipment at INEEL Standards Lab ¹	Flow rate 7 gpm, accuracy +/- 0.5 gpm
Concentrated nitrate brine solution inlet flow rate to biological FFR system	Critical	Volumetric flow rate instrument, corrected for density	Calibrated using in-line 0.25% flow standard and read with NIST traceable test equipment	Before and field test series, scheduled verification of test equipment at INEEL Standards Lab ¹	Flow rate 4 gpm, accuracy +/- 0.5 gpm
Biological FFR process temperature - inlet and outlet	Noncritical	Type T, 1/8", enclosed thermocouple, readings taken with NIST traceable test equipment, curve fit for type T TC	Element characterized to +/- 1 EC using lab standard and referenced to IPTS-68- microvolt tables	Certified to +/-1 EC, scheduled verification of test equipment at INEEL Standards Lab ¹	Inlet and outlet 0 - 50 EC +/- 1 EC
Biological FFR biomass waste measurements	Critical	Gram weight scale and 200-lb capacity scale	Manufacturer's standard procedure performed by INEEL NIST Standards Lab	Before and after the FFR test series	0 - 50 grams +/- 0.5 gram 20-200 lbs +/-0.5 lbs
¹ The standards used for calibration of equipment at MSE facility are verified by the INEEL Secondary Standards Lab on a routine, scheduled basis.					

Biodenitrification of Concentrated Nitrate Brine

4 Week Continuous (Week 1, Day 1)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Wk 1,Day 1,Hr 1		7	500 mL	Temperature, Flow, pH	Field										Field pH-1
Wk 1,Day 1,Hr 1		8	500 mL	Temperature, pH	Field										Field pH-1
Wk 1,Day 1,Hr 1		10	500 mL	Temperature, pH	Field										Field pH-1
Wk 1,Day 1,Hr 1	FFR-B-3001	7	500 mL	Chloride, Sulfate, Alkalinity	Lab		4°C								Lab
Wk 1,Day 1,Hr 1	FFR-B-3002	8	500 mL	Chloride, Sulfate, Alkalinity	Lab		4°C								Lab
Wk 1,Day 1,Hr 1	FFR-B-3003	10	500 mL	Chloride, Sulfate, Alkalinity	Lab		4°C								Lab
Wk 1,Day 1,Hr 1	FFR-B-3004	7	500 mL	Nitrate/Nitrite-N, Ammonia	Lab	H2SO4	4°C								Lab
Wk 1,Day 1,Hr 1	FFR-B-3005	8	500 mL	Nitrate/Nitrite-N, Ammonia	Lab	H2SO4	4°C								Lab
Wk 1,Day 1,Hr 1	FFR-B-3006	8	500 mL	Nitrate/Nitrite-N, Ammonia	Lab	H2SO4	4°C								Duplicate
Wk 1,Day 1,Hr 1	FFR-B-3007	10	500 mL	Nitrate/Nitrite-N, Ammonia	Lab	H2SO4	4°C								Lab
Wk 1,Day 1,Hr 1	FFR-B-3008	8	250 mL	Ortho Phosphate	Lab		4°C								Lab
Wk 1,Day 1,Hr 1	FFR-B-3009	8	50 mL	Methanol or TOC & Flow Rate	Lab		4°C								Lab
Wk 1,Day 1,Hr 1	FFR-B-3010	7	500 mL	Cations-Ca, Mg, K, Na	Lab	HNO3	4°C								Lab
Wk 1,Day 1,Hr 1	FFR-B-3011	8	500 mL	Cations-Ca, Mg, K, Na	Lab	HNO3	4°C								Lab
Wk 1,Day 1,Hr 1	FFR-B-3012	10	500 mL	Cations-Ca, Mg, K, Na	Lab	HNO3	4°C								Lab
Wk 1,Day 1,Hr 1	FFR-B-3013	8	100 mL	Acridine Orange Bacteria Ct.	Lab		4°C								Lab
Wk 1,Day 1,Hr 1	FFR-B-3501	7	100 mL	Nitrate (300 mg/L)	Field										Field Nitrate-3
Wk 1,Day 1,Hr 1	FFR-B-3502	8	100 mL	Nitrate (<1 mg/L)	Field										Field Nitrate-1
Wk 1,Day 1,Hr 1	FFR-B-3503	8	100 mL	Nitrite (0.05 mg/L)	Field										Field Nitrite-1
Column 1 = Sample Time 2 = Sample Number 3 = Sample Port 4 = Sample Size 5 = Sample Analysis 6 = Sampled For 7 = Preservative To Add 8 = Storage Temp 9 = Temp (EC) 10 = Inlet Flow (gpm) 11 = pH Value 12 = Nitrate-Nitrite 13 = Sampled Time 14 = Sampled Date 15 = Initials 16 = Analysis Procedure															

Figure 7-1. Sample of data record for field sampling.

Biodenitrification of Concentrated Nitrate Brine Equipment Calibration Data

4 Weeks Continuous (Week 1, Day 1)

pH Meter	Value Of	Buffer	Buffer	Time	Date	Initials	Calibration
3-Point Cal	Buffer	Accuracy	Lot ID Number				Procedure
High End Buffer							pH Test 2
Mid-Range Buffer							pH Test 2
Low End Buffer							pH Test 2

pH Meter	Value Of	Buffer	Buffer	Time	Date	Initials	Calibration
Single-Point Cal	Buffer	Accuracy	Lot ID Number				Procedure
Mid-Range Buffer							pH Test 2

Temperature Measurement Instrument Serial Number and Model Number _____

Temperature Measurement Instrument Calibration Due Date _____

Flow Meter Calibration Due Date _____

Flow Totalizer Reading _____

Figure 7-2. Sample of equipment calibration record.

8. Quality Assurance and Control

8.1 Review of Laboratory Audits

In preparation for Activity III, Project 4, the most recent systems audit and performance audit of the MSE-HKM laboratory were reviewed with the laboratory QA Officer. Nitrate as nitrogen was the most critical analysis for the project; therefore, the review focused on that analysis.

8.1.1 Systems Audit

The most recent systems audit was performed by Joseph Evans, QA Manager of Science Applications International Corporation (SAIC). The evaluation was performed on September 26, 1995, for MWTP Activity III, Project 5--Biocyanide Field Demonstration at Echo Bay/Cove Mine. While the evaluation focused on cyanide analysis, the auto analyzer used for colorimetric cyanide determination was also used for the nitrate-nitrite as nitrogen analysis. The only concern related to auto analyzer use was the absence of a standard time period for color development; the laboratory has since begun to record the amount of time allowed for color development for cyanide analysis. For nitrate-nitrite as nitrogen determinations, there will be no requirement to record the time period for color development.

8.1.2 Performance Audits

The EPA through the State of Montana submitted performance samples to the MSE-HKM laboratory periodically. The results of the most recent nitrate-nitrite as nitrogen performance evaluation sample was approved by the EPA on April 12, 1995. The MSE-HKM laboratory reported a value of 1.93 mg/L nitrate-nitrite as nitrogen, while the accepted value was 1.90 mg/L. The EPA considered any result in the range of 1.62 to 2.19 mg/L acceptable. The result of this performance evaluation sample demonstrated the MSE-HKM laboratory was prepared to perform nitrate-nitrite analysis for MWTP Activity III, Project 4.

8.2 Field Audits

Two field audits were performed: a preevaluation of site activities and a demonstration sampling audit of site activities.

8.2.1 Preevaluation of Site Activities

A preevaluation of site activities was performed on January 9, 1996, and included a review of the following items:

- personnel, facilities, and equipment;
- documentation (chain-of-custody (COC), logbooks);
- calibration of equipment; and
- sampling procedures.

No concerns were identified with the exception of the storage temperature of the refrigerator.

Concern: Because only a crude temperature control was available in the refrigerator where samples could be stored for up to a week, a procedure to verify the refrigerator temperature remained at or below 4 °C was necessary.

Corrective Action: Thermometer or thermocouple

8.2.2 Demonstration Sampling Audit

A review of sampling activities was performed at the Mineral Hill Mine, the demonstration site, on March 14, 1996. Sampling personnel were trained by MSE-HKM laboratory personnel prior to the demonstration. The audit of sampling activities included reviews of the following areas:

- sample logbook;
- sample collection;
- sample labeling; and
- sample packing and transport.

No concerns were identified during the demonstration sampling audit, and only one minor issue regarding logbook information about blank preservation was identified.

8.2.2.1 Sample Logbook

Sampling logbooks contained all of the appropriate information for sample collection and field measurements that were taken. While a specific space was not provided for additional comments or information, sampling personnel made notes in the margins when necessary. The sampling logbook format facilitated review by specifying a space in

which each measurement would be recorded.

Minor Issue: All of the preservatives required for each sample were clearly listed in the sampling logbooks. However, when the logbook was created, the preservative for nitrate-nitrite as nitrogen and ammonia blank samples was incorrectly listed as N/A.

Blank samples should be preserved identically to the original sample associated with the field blank. For nitrate-nitrite as nitrogen analysis, blanks should be preserved with H_2SO_4 to a pH less than 2. Most of the blank preservative entries had been corrected from N/A to H_2SO_4 , and all COC forms listed H_2SO_4 as the sample preservative for the blanks. Therefore, it is assumed that all the blank samples for nitrate-nitrite as nitrogen and ammonia analysis were properly preserved.

8.2.2.2 Sample Collection

Operations personnel were trained by MSE-HKM laboratory personnel to collect samples for the demonstration. During the sampling audit, no concerns were identified regarding sample collection.

8.2.2.3 Sample Labeling

Adhesive sample labels were designed prior to the demonstration. Labels included appropriate spaces for sample date/time, sampler's initials, requested analysis, sample treatment preservation, and sample identification number. No concerns with sample labeling were identified during the sampling audit; however, a suggestion was made to seal the completed label to the bottle with clear tape to avoid smudging of the information written on the label.

8.2.2.4 Sample Packing and Transport

Because the demonstration occurred at a remote mine site, samples were transported to the MSE-HKM laboratory once a week. Samples were stored in a refrigerator at 4 °C at the demonstration site prior to shipment. The most critical holding times were for acridine orange analysis and orthophosphate analysis. These samples were collected on the day the samples were being brought to the laboratory to avoid exceeding holding times. Samples were shipped via ground transportation in sealed coolers filled with blue ice weekly by project personnel. No

concerns were identified in the areas of sample packing and transport.

8.3 Field and Laboratory Data Validation

The stated objectives of the project in the QAPP were to remove and destroy the nitrate in the mine discharge and concentrated brine at a remote mine site and obtain an effluent with less than 10 mg/L nitrate-nitrite as nitrogen while reducing the by-product waste 80% by mass when compared to conventional ion exchange.

All of the field and laboratory data for weekly sampling events from December 1995 to June 1996 has been evaluated to determine the usability of the data. The final project samples were collected on June 24, 1996.

To determine the effectiveness of the EIX and biodenitrification processes being demonstrated, several sampling points were designated, and a variety of analyses were assigned to each point. The analyses to be performed were specified in the project-specific QAPP, and each analysis was classified as critical or noncritical. A critical analysis is an analysis that must be performed to achieve project objectives. A noncritical analysis is an analysis that is performed to provide additional information about the process being tested. Critical analyses for this project are summarized below:

- nitrate-nitrite as nitrogen;
- liquid (brine and mine water) density;
- amount of liquid (brine or mine water) processed; and
- quantity of waste generated.

Noncritical analyses for this project are listed below:

- pH;
- temperature;
- flowrate;
- power consumption;
- total suspended solids (TSS);
- sulfate;
- chloride;
- alkalinity;
- cations (calcium, magnesium, sodium, and potassium);
- total organic carbon (biodenitrification tests)

- only);
- ortho-phosphate (biodenitrification tests only); and
- acridine orange bacteria counts (biodenitrification tests only).

The QC objectives for each critical analysis were outlined in the QAPP and were compatible with project objectives and the methods of determination being used. The QC objectives are method detection limits (MDLs) accuracy, precision, and completeness. Control limits for each of these objectives were established for each critical analysis. For noncritical analyses, QC objectives were determined by using standard guidelines that exist or by applying reasonable control limits to determine the usability of the data.

8.3.1 Validation Procedures

Data that was generated for all critical and noncritical analyses was validated. The purpose of data validation is to determine the usability of all data that was generated during a project. Data validation consists of two separate evaluations: an analytical evaluation and a program evaluation.

8.3.1.1 Criteria for Analytical Evaluation

An analytical evaluation is performed to determine:

- all analyses were performed within specified holding times;
- calibration procedures were followed correctly by field and laboratory personnel;
- laboratory analytical blanks contain no significant contamination;
- all necessary independent check standards were prepared and analyzed at the proper frequency and that all remained within control limits;
- duplicate sample analysis was performed at the proper frequency and that all relative percent differences (RPDs) were within specified control limits;
- matrix spike sample analysis was performed at the proper frequency and that all spike recoveries (%R) were within specified control limits; and
- the data in the report submitted by the laboratory to project personnel can be verified from the raw data generated by the laboratory.

Measurements that fall outside of the control limits specified in the QAPP or for other reasons are judged to be outlier were flagged appropriately to indicate the data is judged to be estimated or unusable. All QC outliers for all sampling events are summarized in Table 8-1. In addition to the analytical evaluation, a program evaluation was performed.

8.3.1.2 Criteria For Program Evaluation

Program evaluations include an examination of data generated during the project to determine:

- all information contained in COC forms is consistent with the sample information in field logs, laboratory raw data, and laboratory reports;
- all samples, including field QC samples, were collected, sent to the appropriate laboratory for analysis, and were analyzed and reported by the laboratory for the appropriate analyses;
- all field blanks contain no significant contamination; and
- all field duplicate samples demonstrate precision of field as well as laboratory procedures by remaining within control limits established for RPD.

Program data that was inconsistent or incomplete and did not meet the QC objectives outlined in the QAPP were viewed as program outliers and were flagged appropriately to indicate the usability of the data. Both the analytical and program evaluations consisted of evaluating the data generated in the field as well as in the laboratory.

8.3.2 Analytical Evaluation

The analytical evaluation of field and laboratory data was initiated in August of 1996.

8.3.2.1 Field Logbook Evaluation

Field data validation began with an examination of the field logbooks that were created for this project. Sampling logbooks were created for each test combination (i.e., conventional ion exchange, EIX using mine water, EIX using brine, biodenitrification using mine water, and biodenitrification using brine). General site logbooks were also created for the three test units being used during the demonstration: conventional

ion exchange, biodenitrification, and EIX. The field logbook typically contains all of the information that is available about fieldwork performed and sample collection activities.

Information about Fieldwork Performed

The general logbooks contained daily logs of fieldwork performed and process measurements taken. The information provided was complete and contained the necessary tank level measurements and waste generation measurements specified in the QAPP. While the entries in the general logbooks were complete and some of the entries were initialed, not all entries were initialed. All logbook entries should be initialed.

Sample Collection Activities

Sampling logbooks contained all of the appropriate information for sample collection and field measurements that were taken. Sampling conditions and information such as weather conditions, date of sampling, time of sampling, and details of fieldwork performed should be specified in the field logbook for each sampling event. Sampling information was complete and accurate for all sampling events. While a specific space was not provided for additional comments or information, sampling personnel made notes in the margins when necessary. The sampling logbook format facilitated review by specifying a space in which each measurement could be recorded; missing information was easy to locate.

All of the preservatives required for each analysis are clearly listed in the sampling logbooks; therefore, it is assumed all of the samples were properly treated/preserved prior to delivery to the appropriate laboratory, with one exception. When the logbook was created, the preservative for nitrate-nitrite as nitrogen and ammonia blank samples was incorrectly listed as N/A. Blank samples should be preserved identically to the original sample associated with the field blank. For nitrate-nitrite as nitrogen analysis, blanks should be preserved with H_2SO_4 to a pH of less than 2. Most of the blank preservative entries had been corrected from N/A to H_2SO_4 . All COC forms contained the correct information about sample preservation for these blanks.

8.3.2.2 Field Data Validation

Field data validation was performed to determine the usability of the data that was generated during field activities. The usability was determined by verifying correct calibration procedures of field instruments were followed. In addition, the QC parameters of precision and accuracy calculated in the field were compared to those specified in the QAPP. Any data that fell outside of the control limits was considered outlier and was flagged appropriately. The following measurements were performed in the field:

- amount of liquid processed (critical);
- quantity of waste generated (critical);
- pH (noncritical);
- temperature (noncritical); and
- power consumption for EIX tests (noncritical).

All instruments used to measure field process variables were calibrated using NIST traceable equipment furnished by the Instrumentation and Control Laboratory of MSE. The test equipment used during the calibration procedures are verified on a routine basis at the Standards and Calibration Laboratories located at the Idaho National Engineering and Environmental Laboratory (INEEL) in Idaho Falls. This is a certified NIST secondary standards laboratory.

Amount of Liquid Processed

The amount of mine water processed was measured using a flow totalizer; the amount of brine or mine water entering the EIX unit or the biodenitrification reactors was determined using flowrate measurements from flow meters and multiplying by the time elapsed between readings. All flow totalizer and flow meter readings were recorded in the general project logbooks and the sampling logbooks. All amount of liquid processed measurements are considered usable.

Methanol was added as a nutrient to the biodenitrification reactors. The flowrate of methanol was to be recorded daily during the biodenitrification tests. Readings were not recorded on May 16 through May 25, 1996, and June 1 through June 7, 1996, for biodenitrification tests using mine water as the influent. Similarly, methanol flow rates were not recorded on May 1 through May 18, 1996; May 21 through May 25, 1996; and May 31 through June 7, 1996, during the

biodenitrification tests using concentrated brine as the influent.

Quantity of Waste Generated

The quantity of waste generated by conventional ion exchange was determined using tank level measurements. Electrochemical ion exchange and biomass wastes were measured by collecting the waste and weighing it in a previously tared waste collection container following testing. All waste generation information for each test system was recorded in the general logbooks, and all data is considered usable.

pH

The pH meter was calibrated using two known buffer solutions that would bracket the measured pH. To determine the accuracy of the pH meter, a third known buffer in the calibration range was measured. Accuracy was defined as the absolute difference between the accepted value of the third known buffer solution and the measured value of the third known buffer solution. Calibration of the pH meter was performed each day pH measurements were taken. All pH data is considered usable.

Temperature

Temperatures of the process inlets and outlets were measured using Type T, one-eighth-inch enclosed thermocouples or mercury thermometers. All temperatures were recorded in the project logbooks at the proper frequency, and all temperature data is considered usable.

Power Consumption

Power consumption of the EIX unit was measured using a BMI PowerProfiler. This unit will print out power consumption data on demand. Power consumption measurements were only necessary on the tests involving the EIX unit. All power consumption measurements are considered usable.

8.3.2.3 Laboratory Data Validation

Laboratory data validation was performed to determine the usability of the data that was generated by the laboratory for the project. The following analyses were performed by the MSE-HKM laboratory:

- nitrate-nitrite as nitrogen (critical);
- liquid density (critical);

- sulfate (noncritical);
- chloride (noncritical);
- ammonia (noncritical);
- alkalinity (noncritical);
- cations (noncritical); and
- ortho phosphate (noncritical).

Total organic carbon analysis was performed at Columbia Analytical Services, Inc., in Kelso, Washington, a subcontract laboratory to MSE-HKM laboratory. Acridine orange bacteria counts were performed at Montana Tech.

Laboratory data validation was performed using the EPA's *Contract Laboratory Program National Functional Guidelines for Inorganics Data Review* (Ref. 7) as a guide, where applicable, to each individual analysis. For critical analyses, the QC criteria outlined in the QAPP were also used to identify outlier data and to determine the usability of the data for each analysis. When data validation was initiated, the MSE-HKM laboratory was not sending sufficient information to perform a complete and thorough data validation. Due to the large volume of data generated for the project, the data validation was performed at the laboratory rather than requiring the laboratory to submit copies of all data generated for the project.

Nitrate-Nitrite as Nitrogen

Nitrate-nitrite as nitrogen analysis was performed at the MSE-HKM laboratory. All of the nitrate-nitrite as nitrogen data is considered usable; however, some data was estimated because continuing calibration verification sample results fell outside the control limits of 90 to 110% specified in the project-specific QAPP for this critical analysis. The laboratory QAPP specifies control limits of 85 to 115% for recovery of calibration verification samples. Because the qualified data was from one analytical run, the out-of-control data was probably an oversight by the laboratory. During future projects, however, the level of data quality that the laboratory must meet for each project must be better communicated to laboratory personnel. Nitrate-nitrite as nitrogen data requiring qualification is summarized in Table 8-1.

Liquid Density

Liquid density analysis was performed at the

MSE-HKM laboratory, and all liquid density data is considered usable. All required QC checks were performed for this critical analysis, and results were within acceptance criteria specified in the QAPP.

Ammonia

All ammonia data generated at the MSE-HKM laboratory is considered usable. Some ammonia data was qualified as estimated due to contamination present in a field blank. Refer to Section 4.3.1 for a discussion of data qualified due to field blank contamination.

Acridine Orange Bacteria Counts

Acridine orange bacteria counts were performed at Montana Tech.

Remaining Analyses

Sulfate, alkalinity, chloride, cations, total organic carbon, and ortho-phosphate data was also reviewed. All data is considered usable and requires no qualification.

8.3.3 Program Evaluation

The program evaluation focused on the following areas:

- COC procedures;
- sampling and data completeness;
- field blanks; and
- field duplicates.

8.3.3.1 COC Procedures
All information provided in the COC forms for this project is complete and accurate, with the following exceptions:

- C The samples collected on May 1, 1996, have the sampling date incorrectly entered as January 5, 1996. The COC forms and the sample logbook should be amended to include the correct date.

C For samples collected on March 21 and 22; April 24; and May 18, 19, 20, 21, 22, and 24, 1996, nitrate analysis was incorrectly requested on the samples instead of the nitrate-nitrite as nitrogen analysis. The laboratory COC for samples collected March 21, 1996, stated the samples were over the holding time for nitrate analysis (48 hours) but were analyzed for nitrate-nitrite as nitrogen, which has a holding time of 28 days. Although the requested analysis should have been nitrate-nitrite

as nitrogen, the laboratory personnel should have realized that the requested analysis was in error because the samples were preserved with H₂SO₄ in the field. Once the nitrate samples are preserved, nitrate and nitrite cannot be determined as individual species. Nitrate-nitrite as nitrogen analysis was within the specified holding time, and the data for the above sampling events is considered usable.

8.3.3.2 Sampling and Data Completeness

All samples that were to be collected were collected when possible. All collected samples were analyzed for the requested analyses on the COC forms. Because the EIX was not able to treat the brine as expected, not all of the tests outlined in the project-specific QAPP were performed. Therefore, not all of the samples that were outlined in the QAPP were collected. However, extra tests of the technology were performed using mine water as the influent.

8.3.3.3 Field QC Samples

All field QC samples were collected at the proper frequency for tests specified in the QAPP; however, during additional tests, field QC samples were not collected. Field QC samples can provide important information about sources of contamination and sampling precision and should have been collected for each sampling event. Because the precision of laboratory analysis was sufficient and the contamination problems in other field and laboratory blanks was not a concern, associated samples were not qualified.

8.3.3.4 Field Blanks

None of the field blanks collected for the project showed significant contamination, with the following exceptions: the field blank for ammonia sampled on April 23, 1996, was above the upper limit of contamination for blanks specified in the QAPP as four times the MDL. Associated samples above the MDL but less than 10 times the contamination concentration were flagged "U" as not detected for ammonia analysis.

Several other blanks also had contamination; however, the associated sample concentrations for nitrate-nitrite as nitrogen analysis were all at least 10 times the contamination found in the blanks. Consequently, the effect of the contamination had no significant impact on the analyte concentrations

for any of the samples; therefore, no action was taken on the following blanks:

- EIXW2059 for nitrate-nitrite as nitrogen analysis sampled April 23, 1996;
- FFRB3161 for nitrate-nitrite as nitrogen analysis sampled June 3, 1996; and
- FFRW3161 for nitrate-nitrite as nitrogen analysis sampled on June 6, 1996.

8.3.3.5 Field Duplicates

Field duplicates showed very good agreement to the original samples, with the following exceptions:

- ammonia duplicate sampled on June 4, 1996, RPD=38.1%; and
- ammonia duplicate sampled on June 7, 1996, RPD=49.8%.

8.4 QA/QC Findings

Experimental results are located in Appendix B. The results of the nitrate testing and other significant results are listed in the following tables.

8.4.1 Conventional Ion Exchange

Seven batches were processed through the conventional ion-exchange equipment to obtain baseline data. Samples were taken at the beginning, middle, and end of each batch.

8.4.2 Biological Denitrification

During biodenitrification tests for both the mine water and the concentrated nitrate brine, samples were taken daily for 28 days. All samples were taken at approximately the same time every day.

8.4.3 Electrochemical Ion Exchange

Originally it was intended to process 14 batches of concentrated nitrate brine through the EIX unit. After two batches, it was determined that EIX was not an appropriate technology for removing nitrate from a chloride solution, and these tests were discontinued. Four batches of raw mine water were run through the EIX unit.

8.4.4 QA/QC Summary

While the majority of the findings of the analytical and program evaluations are minor and can be easily addressed or have already been addressed, several lessons can be learned so that mistakes will not be repeated during future projects. The following recommendations are suggested to

improve future project and program QA/QC.

8.4.4.1 Laboratory QA/QC

QA/QC summaries and raw data were available for review at the MSE-HKM laboratory on request; however, prior to future projects, project personnel should inform any laboratory performing analyses about QA/QC reporting needs (QA/QC summaries and raw data should be attached to the report).

8.4.4.2 Field QA/QC

The standardized logbook format for this project was very useful to the sampling team. In the future, however, preservatives for blank samples should be assigned the same preservative as the original sample.

The project-specific QAPP was endorsed by the EPA QA Office on November 21, 1995, final approval from the EPA Project Officer was not secured until May 27, 1996. The final version of the QAPP was distributed on June 19, 1996, final project samples were collected June 24, 1996. Because final versions of QAPP documents are not always available, draft updates of the QAPP will be provided to field and laboratory personnel during future projects to keep everyone informed of changes that may affect the project. The QAPP should be an integral part of all projects, and the approval process has been expedited by keeping EPA personnel informed what signatures are necessary to finalize the various project QAPPs.

There was a great volume of data generated during this project. While some of the data is considered estimated for various reasons, the fact that all of the data is usable underlines the fact that the data generated for MWTP Activity III, Project 4, is of high quality.

Table 8-1. Summary of qualified data for MWTP Activity III, Project 4.

Date ¹	Sample ID	Analysis	QC Criteria	Control Limit	Result	Flag ²	Comment
4/22/96 4/22/96 4/23/96 4/23/96 4/25/96 4/25/96 4/25/96 4/25/96	EIXW2048-2050 EIXW2051-2053 EIXW2054-2056 EIXW2057,2058 EIXW2060,2069 EIXW2071-2073 EIXW2061-2063 EIXW2064-2066	Ammonia	Field Blank	2 to 4 times MDL (0.2 to 0.4 mg/L)	1.26 mg/L	U	Samples with less than 10 times the contamination concentration in the blank but above the MDL should be flagged "U."
6/2/96	FFRB3152	Nitrate-Nitrite as Nitrogen	Continuing Calibration Verification (CCV)#4	90-110% Recovery	114.2% Recovery	J	Control limit established in QAPP.
6/4/96	FFRB3170 FFRB3171	Ammonia	Field Duplicate	#20% RPD	38.1% RPD	J	Field duplicate results differed significantly enough to flag associated samples "J," as estimated.
6/7/96	FFRW3170 FFRW3171	Ammonia	Field Duplicate	#20% RPD	49.8% RPD	J	Field duplicate results differed significantly enough to flag associated samples "J," as estimated.
6/16/96 6/16/96 6/17/96 6/18/96 6/18/96 6/19/96 6/19/96	EIXW2191 EIXW2194 EIXW2202 EIXW2206 EIXW2209 EIXW2212 EIXW2216	Nitrate-Nitrite as N	Continuing Calibration Verification (CCV)#10	90-110% Recovery	88% Recovery	J	Control limit established in QAPP.
6/20/96 6/20/96 6/20/96	EIXW2220 EIXW2223 EIXW2226	Nitrate-Nitrite as Nitrogen	Continuing Calibration Verification (CCV)#11	90-110% Recovery	88.8	J	Control limit established in the QAPP.
6/19/96 6/19/96 6/20/96 6/20/96 6/20/96	EIXW2215 EIXW2216 EIXW2219 EIXW2220 EIXW2223	Nitrate-Nitrite as Nitrogen	Continuing Calibration Verification (CCV)#12	90-110% Recovery	85.4	J	Control limit established in the QAPP.
¹ Date the samples were collected. ² Data Qualifier Definitions: U-The material was analyzed for but was not detected above the level of the associated value (quantitation or detection limit). J-The sample results are estimated. R-The sample results are unusable. UJ-The material was analyzed for but was not detected and the associated value is estimated.							

9. Discussion

9.1 Ion Exchange Using Nitrate-Selective Resins

The Altair NIX unit was the first equipment to arrive at the demonstration site. Installation was relatively easy, and the unit and support systems were ready for initial checkout testing within 6 days. The Altair representative arrived on site to assist with startup and provide training for operations personnel. On December 4, 1995, the NIX system was started, and initial adjustments were made.

System startup went well. Initial colorimetric testing of the mine water showed nitrate concentrations to be approximately 5 mg/L as NO_3^- -N, which was lower than expected. To make up for this low concentration and load more nitrate ions on the resin, the feed rate was increased from a nominal 10 to 16 gpm. Subsequent colorimetric sampling showed the inlet nitrate concentration remained near the 5 mg/L level while the treated effluent was less than 0.25 mg/L NO_3^- -N.

System startup was followed with a series of shakedown tests. For this series of tests, the service mode timing was changed from 22 to 46 hours. This was done to compensate for the low nitrate level in the mine water. The regeneration and backwash modes remained at the 2-hour duration. This series of tests was conducted to establish an understanding of how efficient the system would be and if additional service or regeneration timing adjustments were necessary. There were five 48-hour batches of mine water processed for this series. The process inlet flow rate was adjusted to approximately 15 gpm for each batch.

During each batch, samples were taken for laboratory analysis. In addition to analyzing the process feed and effluent for nitrate-nitrite as nitrogen, samples were also analyzed for chloride since the Purolite A-520E resin system exchanges chloride for nitrate. By comparing the chloride concentration of the effluent to that of the feed, an indication of nitrate uptake by the resin was estimated. This provided a cross-check of the nitrate removal data. Additional field samples were analyzed on site to watch for indications of

resin nitrate saturation, which would indicate the service mode was too long.

Laboratory results confirmed the field results and showed the ion-exchange system was performing as expected. Table 9-1 is a summary of the five shakedown batch tests conducted between December 5-16, 1995. Nitrate concentration of the regeneration brine was analyzed by the laboratory for each batch and averaged approximately 275 mg/L. The backwash effluent was also analyzed for both chloride and nitrate. These results showed concentrations of 23,600 mg/L chloride and 130 mg/L nitrate-N. Levels of chloride and nitrate in the backwash were not expected to be this high, and a decision was made to include the backwash effluent with the concentrated nitrate brine for further treatment. Changes to the PLC program were made to divert the backwash to the brine holding tanks.

Quality assurance demonstration tests for the NIX unit were conducted between March 27 and April 11, 1996. This series of tests consisted of five batch runs. The service mode duration was set back to the original 22 hours, and the regeneration/backwash mode was set at 2 hours. The mine water inlet flow rate was adjusted to approximately 10 gpm. These values were set to comply with the QAPP and demonstration test plan.

Batch one of the QA test series went as expected with raw mine water inlet flow rates running between 10 and 11 gpm for a total of 12,944 gallons processed. Before batch two was started, it was noted the mine water entering the demonstration building was cloudy and not clear as in the past. The cistern and mine portal were checked to determine the source of the problem, which was found to be melting snow runoff entering the collapsed portal. Action was taken to divert the runoff as much as possible away from the area. Batch two was started in the service mode at 6:00 p.m. at 12 gpm. At 5:30 a.m., the flow rate had diminished to 7 gpm. It was thought at first that the flow meter had failed; however, further investigation proved the resin bed was becoming clogged with silt. By 8 a.m., the flow

rate had reduced to 5 gpm. The system was manually switched into the regeneration mode at 5:50 p.m., about 20 minutes early. The regeneration and backwash modes seemed to clear some of the sediment from the resin bed. The regeneration and backwash flow rates were also reduced below normal. Batch three, four, and five had the same problem. During the dark, the runoff subsided and the water cleared as the temperature fell below freezing. As the daytime temperatures rose above freezing, the water again became turbid. Table 9-2 shows the decrease in total water processed and nitrate brine generated by each batch.

The total quantity of water treated by the NIX system during the entire demonstration period was in excess of 620,000 gallons.

9.1.1 Data Interpretation

The conventional ion-exchange system proved to be very effective for nitrate removal. As can be seen from the laboratory analysis (Appendix B), the nitrate level was reduced to below the required drinking water standard of 10 mg/L NO_3^- -N, and the nitrate removal percentage was consistently better than 95% throughout the demonstration. Only two of the samples were below the 95% removal level but still remained relatively high at 79.8 and 88.6%. Also, in both cases, the effluent nitrate concentrations were reduced below the required 10 mg/L NO_3^- -N to 2.7 and 4.0 respectively.

Nitrate concentrations in the inlet stream, for samples taken from March 27 until April 3, 1996, remained fairly steady with values ranging between 10.3 and 17.8 mg/L NO_3^- -N. The effluent nitrate concentration averaged well below 1 mg/L NO_3^- -N during this period. Samples taken after April 3 showed a rise in inlet concentrations to values over 30 mg/L NO_3^- -N. This rise in inlet concentration had little effect on nitrate removal performance. The percentage of removal remained consistently above 95%, and the effluent concentrations were reduced to 1 mg/L NO_3^- -N or lower in all but one of the samples.

Costs associated with operation of the ion-exchange unit are summarized in Table 9-3. Replacement of the Purolite A-520E resin accounts for over half of the operational cost for

the unit. Other costs associated with maintenance, electrical, and initial capital are all relatively low. The overall operational cost per gallon of water treated was only \$0.00276. However, these costs do not account for secondary treatment of the concentrated brine produced during regeneration.

9.1.2 Technology Discussion

The ion-exchange technology performed as well as expected for treating nitrate-laden water at the Mineral Hill Mine. It was very effective in reducing nitrates to well below the required level at concentrations up to 35 mg/L NO_3^- -N. The system performed well throughout the demonstration, even during periods of poor water conditions and silting of the resin beds.

9.2 Biological Denitrification

The biological denitrification system consisted of two units. The first was a biodenitrification unit already set up at the Mineral Hill Mine that had been in operation for approximately 1 year. The reactors were designed and fabricated for work that was not related to this project and consisted of biodenitrification reactors in parallel capable of processing approximately 7 gpm. These reactors were used for the raw mine water portion of the demonstration. The QA demonstration test series using raw mine water was carried out over a 4-week period between May 15 and June 12, 1996.

The second unit consisted of biodenitrification reactors created to process the concentrated brine from the ion-exchange technology. Both units were similar in design and used the same heterotrophic organisms to destroy nitrates. This system was inoculated with bacteria from the existing reactors, and a 6-week conditioning period was allowed for sufficient growth in the reactor. The QA test series for the concentrated brine was conducted between May 13 and June 9, 1996.

9.2.1 Data Interpretation

The use of biodenitrification produced mixed results for removal of nitrates. When used to treat raw mine water, the percent of nitrate removal ranged from 31.3 to 64.7; however, in most of the samples, the level of nitrates in the effluent were still above the required 10 mg/L NO_3^- -N. The data also showed large fluctuations in the removal percentage even though the inlet nitrate concentrations remained fairly steady.

The performance of the biodenitrification reactors in treating concentrated brine from the ion-exchange unit was far better than when used to treat raw mine water. The amount of nitrate removal averaged 93% throughout the demonstration with most of the data indicating removal efficiency of greater than 99%. However, from May 17 to May 20, the removal percentage dropped to around 25%. This sharp decrease may be the result of dirty mine water caused by mine drilling that was occurring at the time. The water was very turbid and muddy during this period, and the nitrate concentrations in the feed water increased to over 600 mg/L NO₃-N. From May 21 to June 3, 1996, the results were again good. The percent removal was consistently close to 100 for most of the samples taken, and the nitrate level was reduced far below the desired level in all but one case. Samples taken after June 3 showed a decrease in nitrate removal with effluent nitrate concentrations far exceeding 10 mg/L NO₃-N.

The increase in nitrate concentrations on June 4 seems to be caused by an insufficient carbon addition to the denitrification system. On average, the total organic carbon that was supplied as methanol decreased from 464 mg-carbon per liter (mg-C/L) in the inlet to 109 mg-C/L in the effluent. The inlet value for the sample taken on June 4 was only 77 mg-C/L. The reduction in carbon was caused by a metering pump failure. This level of carbon could not reduce the high nitrate concentration in the inlet stream. However, the samples still showed high removal percentages during this period.

9.2.2 Technology Discussion

Overall, the biodenitrification system removed nitrate and nitrite compounds very effectively when used in conjunction with ion exchange. The nitrate removal percentage was consistently high, and the level of nitrates in the effluent stream was reduced to below the required 10 mg/L for most of the demonstration. Problems with dirty mine water were encountered; however, the system still performed well under these conditions.

9.3 Electrochemical Ion Exchange

The EIX unit arrived at the site on March 7, 1996, and installation of the unit began that day. Installation of the unit went fairly quickly, and initial

adjustments were made to the system before the test series were begun.

The QA demonstration test series for the concentrated brine was performed between March 19-22, 1996. Two separate batch runs were performed at flowrates between 0.5 and 1 gpm. The second batch series was delayed because of failure of the anolyte pump and resulting readjustment of the system before testing could continue. Throughout the two batches, electrical measurements were taken to determine the electrical costs associated with the EIX unit. A total of 950 gallons of concentrated nitrate brine were treated during the two batches.

The QA demonstration test series for the raw mine water began on March 27, 1996, after another period of optimization. Problems with dirty mine water caused some delay during the optimization, and new filters were added to the process. The demonstration consisted of four continuous runs, each under different conditions, the first being a 96-hour run. Electrical measurements were also taken for this part of the demonstration as well. Problems with dirty mine water continued to hamper the demonstration throughout the length of the tests and caused problems with consistent feed water flowrates to the unit. Several different filter sizes and combinations were tried in order to alleviate the problem.

9.3.1 Data Interpretation

Use of the EIX unit for nitrate removal displayed poor results when used for treating both raw mine water and the concentrated brine solution. Laboratory analysis showed limited success at the beginning of the raw mine water treatment demonstration, with nitrate removal at around 80% for the first day. The value quickly dropped to around zero and remained low throughout the rest of the demonstration. Similar results were achieved when the unit was used to treat the concentrated brine solution. The unit removed little or no nitrate throughout most of the demonstration.

The electrical power consumption data collected during the EIX demonstration runs are presented in Table 9-4. Electrical consumption was measured and recorded on a chart by a monitoring

device supplied and operated by MSE for the entire treatment cycle (nitrate removal and resin regeneration/nitrate destruction).

The power consumption numbers presented in Table 9-1 appear to be very favorable. However, when viewed in light of the poor nitrate removal achieved (particularly as reflected by the laboratory analysis) the power consumption data is of little value.

9.3.2 Technology Discussion

The use of EIX was ineffective in treating the nitrate-laden stream at the Mineral Hill Mine. However, several factors were identified by Selentec that unfavorably influenced the test results. The nitrate-specific resin was overwhelmed by the very high chloride concentrations (13,400 to 15,600 mg/L) of the regenerant brine solution. This inhibited the ability of the resin to remove nitrates from the brine solution. The residual chlorides left in the resin after the brine runs continued to cause complications with EIX operation. The most obvious problem was during regeneration of the cell. When these chloride ions were released from the resin, low concentrations of hydrochloric acid and chlorine gas were generated. This undesirable side effect of the brine run persisted through several regeneration cycles following raw mine water treatment runs.

The most consistent and severe problem that was faced during the EIX demonstration was the silt in the raw mine water. Initial shakedown runs were performed with unfiltered raw mine water. When the problem of the mud in the water was first recognized, a small filter was installed. The system was operated with an 80-micron filter in line. When a 22-micron filter was used in place of the 80-micron filter, it plugged rapidly, indicating significant amounts of silt were allowed to enter the system by the 80-micron filter. Because flow could not be maintained through the 22-micron filter for more than a few minutes (often less than 15 seconds), two larger filters were installed in parallel upstream from the small filter. Cartridges (50-micron) were placed in the large filters, which allowed the mine water to flow through the 22-micron filter for up to 4 hours. It was discovered at one point that one of the 22-micron filters had a tear in it which allowed mud to enter the system

for at least 4 hours. The system was shut down, drained, and flushed. Mud was discernable in the flush water after having drained the system, and when the system was restarted, mud was visible for several minutes in the water passing through the flow meters. In an attempt to improve the run time between cleaning the 22-micron filter, the 50-micron filters were replaced by 30-micron filters. Some slight improvement in the performance of the 22-micron filter was noticed; however, the fact that there was a significant amount of silt between 30 and 22 microns indicates that there was likely a significant amount of silt less than 22 microns that was being allowed to enter the system. Eventually a large 5-micron filter was placed in line between the 30-micron and the smaller 22-micron filter.

Silt or mud allowed to enter the EIX unit can have several detrimental effects. The tightly packed resin columns and the scrubbing pad material used to prevent loss of the resin can act as mechanical filters causing mud to build up in the unit over time. This could have led to the observed increases in pressure drop through the unit, which hindered Selentec's ability to achieve reasonable mine water flow rates. Additionally, this filtration effect left mud on the outside of the resin, reducing resin capacity. Another effect of mud in the unit has to do with the macroporosity of ion-exchange resins; small silt particles could enter the interior of resin beads and clog the pores. This led to still further reduction in resin capacity. While flushing the system with clean water did alleviate some of the external effects, the internal effects were permanent. Finally, mud coated the surfaces of the membranes that separate the resin from the electrode compartments, inhibiting the flow of anions across the membrane and reducing regeneration efficiency.

Another difficulty faced during the demonstration was the unidentified "white suspended matter" in the mine water. The field observations of this material led to some concern. When a raw mine water sample was collected and allowed to stand several hours, the material did not settle out, and the water had a milky white haze. This suggests the material has a very small particle size that could not be captured by the 22-micron filter and would be small enough to enter the pores of the resin. Another observation made was that this suspended white material when combined with the

mud on the 22-micron filter formed a sticky substance that was difficult to remove from the filter. It appeared the material that passed through the filter into the system formed this sticky substance in the unit, exacerbating the pressure drop and capacity problems already caused by the mud.

Resin fouling and membrane plugging due to dirty mine water greatly reduced the effectiveness of the EIX technology. These problems will need to be overcome before EIX can successfully be used to treat a nitrate-laden mine water.

Table 9-1. Nitrate ion exchange shakedown test results.

	Ammonia		Chloride		Nitrate/ Nitrite-N		Sulfate		Calcium		Magnesium		Potassium		Sodium	
	in	out	in	out	in	out	in	out	in	out	in	out	in	out	in	out
Min	0.1	0.1	<5	34	4.0	0.1	53.0	9.0	49.0	48.6	23.6	23.2	24.1	24.1	12.8	12.7
Max	0.5	0.4	<5	197	10.2	0.4	87.0	19.0	62.2	71.7	27.3	27.4	27.9	27.9	18.3	16.3
Mean	0.2	0.2	5.0	116	6.9	0.2	65.5	13.4	54.9	56.7	25.3	25.1	25.9	25.7	13.8	14.1
Std	0.1	0.1	.01	61.4	2.4	0.1	11.4	3.7	4.3	6.1	1.3	1.4	1.2	1.3	1.4	1.2
Note: All results are in mg/L.																

Table 9-2. Nitrate ion exchange QA test series.

Batch Number	Flow Rate	Water Processed	Nitrate Brine Generated
Batch #1	10-11 gpm	12,944 gal	609.5 gal
Batch #2	5-12 gpm	10,295 gal	589.8 gal
Batch #3	8-11 gpm	11,434 gal	472.4 gal
Batch #4	7-13 gpm	11,207 gal	343.1 gal
Batch #5	6.7-12 gpm	10,879 gal	

Table 9-3. Ion-exchange unit operational cost.

Parameter	Original Purchase Price	Daily Operational Cost (24 Hrs)	Operational Cost Per 1,000 Gallons Treated
Ion Exchange Unit	\$28,000 10 Year Life	\$7.67	\$0.64
Resin Purolite A-520E	\$1500 Projected Change-out @ 1 Million Gallons	\$18.00	\$1.5
Electrical	\$0.075/KW hr. Avg Used 3 KW hr.	\$5.40	\$0.45
Maintenance	None Required Projected for Life of Unit \$740 Year	\$2.03	\$0.17
Totals		\$33.10 Single 24-hr Batch Treated 12,000 gal	\$2.76

Table 9-4. EIX power measurement for MWTP demonstration.

Batch	Start Date	Stop Date	Kwhr	Cost	Gal. Treated	Cost/ Kilogallon
Brine 1	3/19/96	3/21/96	23.36	\$2.10	281	\$7.48
Brine 2	3/22/96	3/25/96	15.85	\$1.43	252	\$5.68
RMW 1	4/17/96	4/22/96	57.36	\$5.16	15886	\$0.32
RMW 2	4/22/96	5/4/96	27.88	\$2.51	20319	\$0.12
RMW 3	5/6/96	5/10/96	0.17	\$0.02	6887	\$0.00
RMW 4	6/8/96	6/26/96	19.30	\$1.74	31772	\$0.05

10. Recommendations

10.1 Ion-Exchange Technology

Ion-exchange technology using nitrate-selective resins is a well-developed technology and is widely used throughout the industrial community. For this reason, it is not recommended to evaluate ion exchange further as a stand-alone technology. However, it may prove useful to combine this with other innovative technologies that show promise for destruction of concentrated nitrate brine solution. If future studies of ion-exchange technology are conducted, they should focus on optimizing the process with an emphasis on maximizing the nitrate concentration and minimizing the chloride level.

10.2 Biological Denitrification Technology

Biological denitrification technology met the project goals during most of the demonstration. There is potential for this technology to be successfully used in many nitrate removal applications. The occasions when the biodenitrification unit failed to meet project goals were explainable and could likely be corrected with design refinements. It is recommended that future work be focused on performance evaluation with emphasis on reactor size with relation to nitrate concentrations, reactor biomass reduction, or flushing method. It is further recommended that other types of reactor substrates be investigated.

10.3 Electrochemical Ion-Exchange Technology

Electrochemical ion-exchange is an innovative technology that showed promising results in the laboratory but was not successful in the field. During the mine water demonstration, silt was introduced into the process water from the snow melt spring runoff. Prefiltering removed particles larger than 5 microns. Particles smaller than this may have been responsible for reducing nitrate migration by obstructing flow through the membrane and also contaminating the resin. Future designs should incorporate a system to periodically backflush the membranes and the resin beds. Recommendations for future testing would include increasing the size of the unit proportional to the nitrate concentration of the process stream and developing an off-line system to backflush the membranes and resin beds. Another recommendation would be to find a resin able to remove nitrate ions from a concentrated chloride brine solution. Electrochemical ion-exchange technology is interesting and shows promise in certain applications. It is recommended that some of the problems encountered in the field be resolved at bench scale. Following this, pilot-scale demonstrations would be appropriate.

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Appendix A
DOE NEPA Categorical Exclusion

United States Government

Department of Energy

Pittsburgh Energy Technology Center

memorandum

DATE: JAN 07 1994

REPLY TO:
ATTN OF: DI-04 (L. Lorenzi)

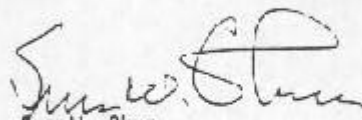
SUBJECT: Section D Determination in Accordance with the Department of Energy's
National Environmental Policy Act Implementing Procedures

TO: Distribution

The purpose of this memorandum is to transmit one Section D Determination for a proposed action involving site characterization, environmental monitoring, and technology feasibility testing on an approach for controlling nitrate-contaminated mine water discharges. The proposed action would be performed at the Mineral Hill Mine near Gardine, Park County, Montana, and at Butte, Silver Bow County, Montana.

This action, under the Mine Waste Pilot Program at the Component Development and Integration Facility, is generally accepted to be within the class of actions that will not have significant impact upon the human environment. This Determination is for a proposed action titled "Nitrate Removal Field Testing."

If there are any questions regarding this Determination, please contact me or Mr. Lloyd Lorenzi at 412/892-6159.


Sun W. Chun
Director

Attachment

Distribution:

Original to PETC EH&S Records Center (5440)
J. Siegel, FE-1
J. Johnson, FE-6
R. Carabetta, PETC
J. Murphy, PETC
E. Ashby, Butte Management Office

CATEGORICAL EXCLUSION DETERMINATION

A. Proposed Action:

Title: Nitrate Removal Field Testing

Location: Jardine, Park County, Montana
Butte, Silver Bow County, Montana

Duration: 36 months

Proposed by: MSE, Inc.

Description:

The proposed action would involve performance testing to determine the technical merit and economic feasibility of candidate technologies for removing nitrate, via reduction to nitrogen and oxygen gases, from mine water. Technologies to be tested would include ion exchange with nitrate selective resin, biological denitrification, and electrochemical ion exchange.

The proposed action would consist of a phased approach for technology testing. Initially, small, skid-mounted units capable of processing up to 10 gallons per minute of water would be assembled and shakedown-tested in an existing building at the Component Development and Integration Facility in Butte.

Upon verification of successful performance, the modular units would be transported to the Mineral Hill Mine in Jardine, Montana, where they would be located in an existing building (Rainbow Building). The units would be variously connected to test the following four treatment methods to reduce nitrate levels from mine water discharges:

- ion exchange followed by biological denitrification for destruction of nitrate in the concentrated solution
- ion exchange followed by electrochemical ion exchange for destruction of nitrate in the concentrated solution
- biological denitrification
- electrochemical ion exchange

At the Mineral Hill Mine, PVC pipe would be installed to intercept mine water flowing at a rate of 7-30 gallons per minute, with a nitrate concentration of up to 30 parts per million, from an inactive portal to an existing percolation pond. Via gravity flow, the installed pipe would divert portal discharge water to the test units in the Rainbow Building. Subsequent to processing through the test units, the treated water would be reintroduced into the

- (g) Sampling and characterization of water effluents, air emissions, or solid waste streams;
- (h) Installation and operation of meteorological towers and associated activities, including assessment of potential wind energy sources;
- (i) Sampling of flora and fauna; and
- (j) Archeological, historic, and cultural resource identification in compliance with 36 CFR Part 800 and 43 CFR Part 7.

83.8 Outdoor ecological and other environmental research (including siting, construction, and operation of a small-scale laboratory building or renovation of a room in an existing building for sample analysis) in a small area (generally less than five acres) that would not result in any permanent change to the ecosystem.

C. Conditions Applicable to the Proposed Action:

1. The proposed action would not threaten a violation of applicable statutory, regulatory, or permit requirements for environment, safety, and health, including requirements of DOE Orders.
2. The proposed action would not require siting and construction or major expansion of waste storage, disposal, recovery, or treatment facilities (including incinerators and facilities for treating waste water, surface water, and ground water).
3. The proposed action would not disturb hazardous substances, pollutants, contaminants, or CERCLA-excluded petroleum and natural gas products that pre-exist in the environment such that there would be uncontrolled or unpermitted releases.
4. The proposed action meets eligibility criteria for environmentally sensitive resources as follows:
 - a. The proposed action would not adversely affect property of historic, archaeological, or architectural significance.
 - b. The proposed action would not adversely affect (1) Federally- or State-listed endangered or threatened species or their habitats or (2) Federally-proposed or candidate species or their habitats.
 - c. The proposed action would not adversely affect floodplains or wetlands.
 - d. The proposed action would not affect natural areas such as Federally- and State-designated wilderness areas, national

percolation pond. The proposed action would not alter either the rate of water discharge from the mine portal or the rate of water inflow to the percolation pond.

Each of the four planned methods for water treatment would be continuously operated for four-week periods during several annual cycles of technology testing over the course a three years period. This approach would provide sufficient operating time to fully assess the technical feasibility of each technology and to evaluate the seasonal effects of natural processes on effectiveness and operability.

Upon completion of testing, the modular units, installed PVC pipe, and all supporting equipment would be removed from the Mineral Hill Mine site.

B. Categorical Exclusions to be Applied (from the Department of Energy's National Environmental Policy Act Implementing Procedures; 10 CFR 1021, Subpart D, Appendix B):

B3.1 Site characterization and environmental monitoring, including siting, construction, operation, and dismantlement or closing (abandonment) of characterization and monitoring devices and siting, construction, and operation of a small scale laboratory building or renovation of a room in an existing building for sample analysis. Activities covered include, but are not limited to, site characterization and environmental monitoring under CERCLA and RCRA. Specific activities include, but are not limited to:

- (a) Geological, geophysical (such as gravity, magnetic, electrical, seismic, and radar), geochemical, and engineering surveys and mapping, including the establishment of survey marks;
- (b) Installation and operation of field instruments, such as stream gauging stations or flow measuring devices, telemetry systems, geochemical monitoring tools, and geophysical exploration tools;
- (c) Drilling of wells for sampling or monitoring of groundwater or the vadose (unsaturated) zone, well logging, and installation of water level recording devices in wells;
- (d) Aquifer response testing;
- (e) Installation and operation of ambient air monitoring equipment;
- (f) Sampling and characterization of water, soil, rock, or contaminants;

parks, national natural landmarks, wild and scenic rivers, coastal zones, State and Federal wildlife refuges, or marine sanctuaries.

- e. The proposed action would not adversely affect prime agricultural lands.
- f. The proposed action would not adversely affect special sources of water (such as Class I groundwater, sole-source aquifers, wellhead protection areas, or other water sources that are vital to the region).
- g. The proposed action would not adversely affect tundra, coral reefs, or rain forests.

D. Determination

I have determined that the proposed action fits the category of actions encompassed by the categorical exclusions, meets the eligibility criteria for the categorical exclusions, and would not present any extraordinary circumstances such that the action might have a significant impact upon the human environment. Therefore, I have determined that the proposed action may be categorically excluded from further review.

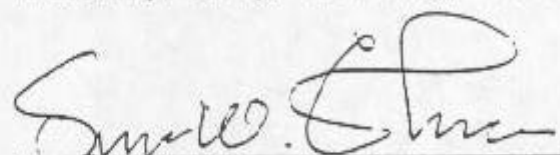
Signature:



Lloyd Lorenzi, Jr.
NEPA Compliance Officer
Pittsburgh Energy Technology Center

Date: 1/6/94

Signature:



Sun W. Chun
Director
Pittsburgh Energy Technology Center

Date: 1/7/94

Appendix B

Laboratory Sample Analysis

Table B-1. Conventional ion exchange of raw mine water.

Batch	Date	Time	Nitrate/Nitrite-N (mg/L)	
			Feed	Effluent
1	3/27/96	4:50 pm	17.5	0.43
	3/28/96	3:30 am	17.1	0.39
	3/28/96	1:00 pm	17.8	0.35
2	4/1/96	6:30 pm	10.3	0.28
	4/2/96	5:30 am	12.4	0.25
	4/2/96	3:20 pm	11.9	0.23
3	4/2/96	6:30 pm	11.9	0.33
	4/3/96	5:30 am	13.2	0.23
	4/3/96	3:00 pm	12.2	0.18
4	4/3/96	6:30 pm	13.4	2.71
	4/4/96	5:30 am	13.6	0.43
	4/4/96	3:00 pm	15.8	0.46
5	4/10/96	9:45 am	20.2	0.51
	4/11/96	9:45 am	20.6	0.37
	4/11/96	6:30 am	23.0	0.47
6	4/15/96	12:00 pm	35.4	4.02
	4/16/96	8:30 am	35.1	0.41
	4/16/96	6:00 pm	38.2	0.33
7	4/17/96	11:00 am	34.7	1.08
	4/17/96	10:00 am	37.4	1.22
	4/18/96	9:00 am	31.4	1.09

Table B-2. Biological denitrification of raw mine water.

Date	Nitrate/Nitrite-N (mg/L)	
	Feed	Effluent
5/16/96	16.4	26.1
5/17/96	25.4	17.1
5/18/96	27.5	18.9
5/19/96	23.1	14.4
5/20/96	21.9	12.6
5/21/96	17.9	11.2
5/22/96	24.0	10.3
5/23/96	27.2	12.3
5/24/96	20.5	11.3
5/25/96	21.8	11.7
5/26/96	26.2	17.2
5/27/96	22.7	13.2
5/28/96	22.2	10.6
5/29/96	27.5	14.5
5/30/96	23.2	8.7
5/31/96	23.6	8.8
6/1/96	26.1	14.8
6/2/96	28.8	13.3
6/3/96	23.8	11.8
6/4/96	27.9	9.9
6/5/96	25.6	10.5
6/6/96	26.7	13.2
6/7/96	27.4	23.1
6/8/96	29.4	12.9
6/9/96	24.1	13.3
6/10/96	26.2	11.5
6/11/96	21.4	11.6
6/12/96	22.4	8.7

Table B-3. Biological denitrification of concentrated nitrate brine.

Date	Nitrate/Nitrite-N (mg/L)	
	Feed	Effluent
5/13/96	296	87.30
5/14/96	267	10.90
5/15/96	305	0.09
5/16/96	273	3.80
5/17/96	674	15.00
5/18/96	651	303.00
5/19/96	629	467.00
5/20/96	428	111.00
5/21/96	388	68.00
5/22/96	363	0.10
5/23/96	365	0.30
5/24/96	325	0.10
5/25/96	376	0.10
5/26/96	344	0.20
5/27/96	357	0.20
5/28/96	334	0.10
5/29/96	327	0.20
5/30/96	344	0.60
5/31/96	397	5.50
6/1/96	339	10.30
6/2/96	388	4.60
6/3/96	393	0.10
6/4/96	397	189.00
6/5/96	340	9.50
6/6/96	382	31.90
6/7/96	406	103.00
6/8/96	342	58.80
6/9/96	365	63.00

Table B-4. EIX of concentrated nitrate brine.

Batch	Date	Time	Nitrate/Nitrite-N		Chloride	
			mg/L		mg/L	
			Feed	Effluent	Feed	Effluent
1	3/19/96	1:00 PM	373	390	13,600	13,700
	3/19/96	5:00 PM	397	377	14,000	13,700
	3/19/96	8:30 PM	384	388	13,400	13,900
2	3/22/96	10:45 AM	315	238	14,600	14,400
	3/22/96	2:15 PM	316	311	15,600	13,300
	3/22/96	6:00 PM	232	331	15,100	15,600

Table B-5. EIX of raw mine water.

Batch	Date	Time	Nitrate/Nitrite-N		Chloride	
			mg/L		mg/L	
			Feed	Effluent	Feed	Effluent
1	4/17/96	1:00 pm	34.4	4.8	14	49
	4/17/96	8:30 pm	34.9	8.0	14	31
	4/18/96	4:00 am	34.5	19.9	14	17
	4/18/96	12:00 pm	34.0	34.9	14	14
	4/19/96	12:00 pm	34.4	35.2	14	14
	4/20/96	12:00 pm	35.7	34.8	14	14
	4/21/96	12:00 pm	35.0	33.3	14	14
2	4/22/96	5:00 pm	28.8	30.8	14	15
	4/23/96	12:00 am	27.6	28.0	13	14
	4/25/96	11:30 pm	29.9	27.7	13	14
	4/25/96	3:30 pm	30.2	29.6	14	17
	4/27/96	8:00 pm	29.9	32.0	18	18
	4/28/96	8:00 pm	33.9	34.3	19	19
	4/29/96	7:30 pm	31.6	31.5	18	19
	4/30/96	7:30 pm	30.9	30.4	19	19
	5/2/96	7:30 pm	32.2	30.9	19	18
	5/2/96	7:30 pm	27.8	31.0	19	20
	5/3/96	7:30 pm	30.8	32.4	19	19
3	5/6/96	8:30 am	29.0	18.4	20	9
	5/6/96	4:30 pm	28.3	28.3	19	19
	5/7/96	12:30 am	26.6	27.1	17	17
	5/7/96	8:30 am	26.6	26.0	23	22
	5/8/96	8:30 am	21.7	24.3	17	18
	5/9/96	8:30 am	0.92	0.84	17	17
	5/10/96	8:30 am	0.63	0.75	16	16
4	6/8/96	12:00:00	29	18.3	19	22
	6/11/96	18:00:00	21.6	8.36	19	25
	6/12/96	00:00:00	24.1	13.3	18	20
	6/12/96	08:00:00	20.5	24	20	18
	6/13/96	08:00:00	25.4	23.6	20	20
	6/14/96	08:00:00	31.4	27.6	20	19
	6/15/96	08:00:00	27.3	30.3	18	19
	6/16/96	08:00:00	26	23.8	18	18
	6/17/96	08:00:00	25.2	24.8	19	17
	6/18/96	08:00:00	28.6	26.2	18	17
	6/19/96	08:00:00	27.4	28	17	18
	6/20/96	08:00:00	28.5	28.2	18	18
	6/21/96	08:00:00	25.4	26.2	19	18
	6/22/96	08:00:00	26.5	25.5	19	18
	6/23/96	08:00:00	25.8	25.6	18	18
	6/24/96	08:00:00	24.8	25.1	18	18